for the different orientation of the cation with respect to the Cl atoms. The Cl triangle of octahedron (I) [Cl(4)] close to the cation has nearly the same orientation as the N triangle of the cation, while the related triangle of octahedron (II) [Cl(3)] is twisted by 60° (Fig. 2). This arrangement may be the reason for charge-transfer contacts and the observed properties of colour and stability. A more accurate investigation with respect to electron density distributions has been started. Compounds containing the $NbCl_6^-$ or the $TaCl_6^-$ ion such as the K salt are colourless solids. The $[C_3\{N(CH_3)_2\}_3]^+.ClO_4^-$ (Ku & Sundaralingam, 1972) is also colourless. So the intense blue colour of compound (1) and the intense red colour of compound (2) can be attributed to an interionic outer-sphere charge-transfer transition. This conclusion is supported by the observation that the colour vanishes in solution and by the value of the Cl—N distance of 3.59 Å, which is in the typical range for interionic charge-transfer salts. A detailed publication with respect to the theoretical approach to the effect is in preparation.

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Structures of Methyl- and Benzyl(η^1-azaferrocene)cobaloximes

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Abstract. (I) (η^1-Azaferrocene-*N*)bis(dimethylglyoximato-*N*,*N'*)(methyl)cobalt(III), $[Co(FeC_9H_9N)(C_4H_7N_2O_2)_2(CH_3)]$, $M_r = 491.22$, monoclinic, $P2_1/c$, $a = 8.539$ (3), $b = 17.957$ (7), $c = 14.215$ (6) Å, $\beta = 102.54$ (4)°, $V = 2127.7$ Å^3, $Z = 4$, $D_x = 1.533$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 14.64$ cm^{-1}, $F(000) = 1004$, room temperature, final $R = 0.039$, $wR = 0.040$ for 2948 observed reflections. (II) (η^1-Azaferrocene-*N*)benzylbis(dimethylglyoximato-*N*,*N'*)cobalt(III), $[Co(FeC_9H_9N)(C_4H_7N_2O_2)_2(C_7H_7)]$, $M_r = 567.31$, triclinic, $P\bar{1}$, $a = 10.619$ (4), $b = 11.353$ (4), $c = 12.693$ (5) Å, $\alpha = 85.43$ (4), $\beta = 119.48$ (5), $\gamma = 109.07$ (4)°, $V = 1252.87$ Å^3, $Z = 2$, $D_x = 1.503$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 12.49$ cm^{-1}, $F(000) = 588$, room temperature, final $R = 0.049$, $wR = 0.056$ for 2285 observed reflections. This work presents X-ray structures of two binuclear cobaloximes, containing axially coordinated azaferrocene. Co—N(ax.) and Co—C bond lengths are discussed and compared with those of other analogs. The structural *trans* effect of (I) and (II) is analyzed in terms of σ-donor power and π-acceptor properties of azaferrocene.

Introduction. The structural and reaction chemistry of alkylcobaloximes attracts great interest since these complexes are considered as models for coenzyme B_{12} (Bresciani Pahor, Forcolin, Marzilli, Randaccio, Summers & Toscano, 1985; Randaccio, Bresciani Pahor, Zangrando & Marzilli, 1989; Bresciani Pahor, Geremia, Lopez, Randaccio & Zangrando, 1990) and set up useful sources of alkyl radicals *via* Co—C bond homolysis (Pattenden, 1988; Giese, Hartung, He, Hüter & Koch, 1989). Recently, binuclear alkylcobaloximes containing azaferrocene (AF) [(η^5-2,4-cyclopentadien-1-yl)(η^5-1*H*-pyrrol-1-yl)iron] as axial ligand have been synthesized (Zakrzewski & Giannotti, 1990), confirming that the σ–π bridging is a common feature of heterocyclic ligands (Mathey, 1987; Zakrzewski, 1990). The crystal structures of the two alkyl(η^1-azaferrocene)cobaloximes (I) and (II) were determined in order to provide a better understanding of N-ligating properties of AF. This

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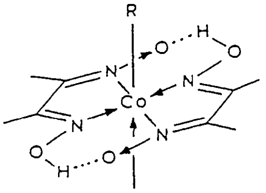
ligand may be regarded as an organometallic analog of pyridine in a similar way to ferrocene being considered as an organometallic analog of benzene.



(I) R = Me, L = AF

(II) R = φ-CH$_2$, L = AF

Experimental. Red prismatic single crystals, 0.20 × 0.20 × 0.8 mm for (I) from methanol, 0.30 × 0.10 × 0.03 mm for (II) from 2-propanol–water solution, were sealed in Lindemann-glass capillaries with mother liquor. D_m not measured. Graphite-monochromated Mo $K\alpha$ radiation, four-circle Philips PW 1100 diffractometer, θ–2θ scan technique, unit-cell dimensions refined from setting angles of 25 reflections ($10 < \theta < 15°$). Three standard reflections measured every 3 h to monitor instrument and crystal stability, no decay. Compound (I): 8727 measured intensities collected up to $2\theta = 50°$, $-10 \leq h \leq 10$, $-22 \leq k \leq 22$, $0 \leq l \leq 17$, 3484 unique reflections, $R_{\rm int} = 0.02$, 2948 reflections considered as observed with $I \geq 3\sigma(I)$, $\sigma(I)$ derived from counting statistics; Lorentz and polarization effects and empirical absorption [maximum/minimum transmission factors 0.9/1.3, (Walker & Stuart, 1983)] corrections. Compound (II): 4394 reflections collected up to $2\theta = 50°$, $-12 \leq h \leq 10$, $-13 \leq k \leq 13$, $0 \leq l \leq 14$, 4302 unique, 2285 considered as observed [$I \geq 3\sigma(I)$]; Lp and empirical absorption (maximum/minimum transmission factors 0.9/1.4) corrections. Structure resolution by direct methods using *SHELXS*86 (Sheldrick, 1986) and refinement by full-matrix least-squares method using *SHELX*76 (Sheldrick, 1976), with anisotropic temperature factors; function minimized $\sum w(|F_o| - |F_c|)^2$. Compound (I): $w = 1/[\sigma^2(F_o) + 0.000548F_o^2]$; all H atoms located on difference Fourier maps and refined with isotropic thermal parameters equal to those of the bonded atoms; the axial methyl group and one of the four equatorial methyl groups are disordered; partial occupancy factors refined to $\frac{1}{3}$ and $\frac{2}{3}$ for each; H atoms for methyl groups were refined with constraints on the atom–atom distances (Waser, 1963); final $R = 0.039$, $wR = 0.040$ (for 2948 reflections and 358 parameters), $(\Delta/\sigma)_{\rm max} = 2.82$, minimum and maximum peaks in ΔF map were -0.32 and 0.24 e Å^{-3}. Compound (II): refinement of phenyl, cyclopentadienyl and pyrrolyl rings performed as rigid groups to take into account the rather low number of data *versus* the number of parameters, $w = 1/[\sigma^2(F_o) + 0.001F_o^2]$; calculable H atoms introduced in their theoretical positions (C—H = 1 Å) and assigned the equivalent isotropic thermal factors of the bonded C atoms; the two H atoms of the equatorial dioximate fragment were located on difference Fourier maps and refined; H atoms of methyl groups, located on Fourier difference series, were refined with constraints on the atom–atom distances; final $R = 0.049$, $wR = 0.056$ (for 2285 reflections and 330 parameters), $(\Delta/\sigma)_{\rm max} = 0.54$; minimum and maximum peaks in ΔF map were -0.17 and 0.14 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final atomic parameters are given in Table 1, bond distances, angles and hydrogen-bond geometry in Table 2.* Figs. 1 and 2 give perspective views of the compounds with the numbering schemes.

Discussion. The coordination around the Co atoms is nearly octahedral. Co is coordinated, in the equatorial plane, by four N donors of the dimethylglyoximato (DH) units and axially by the N atom of the η^5-pyrrolyl ring of azaferrocene ligand L and the C atom of alkyl group R. The four N atoms of DH are truly coplanar within ±0.003 (1) Å for (I) and ±0.009 (6) Å for (II), the Co atom being displaced by 0.055 (1) and 0.033 (1) Å respectively for (I) and (II) from their plane, towards the AF ligand. The dihedral angle α between the mean planes of the DH moieties is +5.6 and +1.7° for (I) and (II), respectively (the positive sign of α denotes a bending towards the alkyl group).

The geometry of the two equatorial units agrees with that usually reported in structures of bis(DH)-cobaloxime derivatives. However, the mean Co—N(eq.) bond length of 1.877 (3) Å for (I) and 1.878 (6) Å for (II) is slightly shorter than usual: 1.890 (1) Å, mean of 306 averaged measurements (Randaccio, Bresciani Pahor, Zangrando & Marzilli, 1989).

In both structures intramolecular hydrogen bonds are observed in the equatorial plane of the macrocycle. In (I) (Fig. 1) the arrangement of protons corresponds to local symmetry C_{2h}, as is seen in the methyl(Co)(DH)$_2$(imidazole) derivative (Pattabhi, Nethaji, Gabe, Lee & Le Page, 1984) or in the benzyl(Co)(DH)$_2$(pyridine) complex (Bresciani Pahor, Randaccio, Zangrando & Antolini, 1988). In (II) (Fig. 2) the H atom cannot be unambiguously

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54815 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10$) *for non-*H *atoms, with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}
(I)				
Co	1647 (1)	3763 (1)	7705 (1)	27 (1)
N(1)	3559 (4)	3410 (2)	7413 (2)	41 (3)
N(2)	1093 (4)	3856 (2)	6358 (2)	49 (3)
N(3)	2175 (4)	3605 (2)	9044 (2)	37 (3)
N(4)	−304 (4)	4060 (2)	7983 (2)	41 (3)
C(1)	3633 (6)	3376 (2)	6515 (2)	53 (4)
C(2)	2164 (6)	3636 (3)	5886 (3)	60 (5)
C(3)	1060 (5)	3760 (2)	9504 (3)	46 (4)
C(4)	−412 (5)	4029 (2)	8877 (3)	49 (4)
C(5)	752 (6)	2719 (3)	7559 (3)	51 (4)
C(11)	5039 (8)	3098 (3)	6158 (5)	84 (7)
C(22)	1875 (10)	3635 (4)	4810 (4)	100 (9)
C(33)	1270 (9)	3638 (4)	10557 (4)	84 (7)
C(44)	−1899 (7)	4231 (4)	9212 (5)	83 (7)
O(11)	4840 (4)	3196 (2)	8096 (2)	55 (3)
O(22)	−349 (4)	4105 (2)	5887 (2)	74 (4)
O(33)	3603 (4)	3344 (2)	9502 (2)	52 (3)
O(44)	−1553 (3)	4293 (2)	7302 (2)	64 (3)
Fe	3661 (1)	5620 (1)	7297 (1)	41 (1)
N(60)	2437 (3)	4837 (2)	7897 (2)	33 (2)
C(61)	1501 (5)	5473 (2)	7643 (3)	51 (4)
C(62)	2255 (7)	6087 (3)	8135 (4)	64 (5)
C(63)	3696 (7)	5840 (3)	8713 (3)	58 (5)
C(64)	3795 (5)	5078 (2)	8562 (3)	40 (3)
C(71)	5830 (6)	5673 (3)	6912 (4)	67 (6)
C(72)	4838 (9)	5204 (3)	6309 (5)	84 (7)
C(73)	3518 (9)	5591 (6)	5865 (4)	102 (10)
C(74)	3695 (13)	6327 (6)	6204 (8)	134 (12)
C(75)	5144 (11)	6353 (3)	6836 (6)	95 (8)
(II)				
Co	4679 (1)	7551 (1)	7516 (1)	34 (1)
N(1)	3194 (7)	7532 (6)	7923 (5)	58 (1)
N(2)	5030 (7)	9272 (5)	7614 (5)	56 (8)
N(3)	4413 (6)	5831 (5)	7486 (5)	49 (8)
N(4)	6212 (6)	7594 (6)	7152 (5)	51 (8)
C(1)	3127 (9)	8598 (8)	8110 (7)	65 (11)
C(2)	4199 (9)	9654 (7)	7902 (7)	64 (11)
C(3)	5268 (8)	5484 (7)	7223 (7)	58 (10)
C(4)	6345 (8)	6518 (7)	7015 (6)	58 (10)
C(11)	2061 (11)	8779 (10)	8512 (9)	99 (16)
C(22)	4333 (13)	10995 (8)	8003 (10)	102 (17)
C(33)	5228 (11)	4154 (8)	7200 (10)	96 (16)
C(44)	7504 (12)	6422 (10)	6741 (10)	106 (17)
O(11)	2281 (6)	6465 (5)	8074 (5)	83 (9)
O(22)	6082 (6)	10128 (4)	7398 (5)	76 (8)
O(33)	3362 (6)	4986 (4)	7735 (5)	77 (8)
O(44)	7110 (6)	8654 (5)	7002 (5)	70 (7)
C(5)	6107 (8)	7662 (7)	9357 (6)	61 (10)
C(51)	7510 (5)	7345 (4)	9779 (4)	48 (9)
C(52)	8848 (5)	8253 (4)	9911 (4)	64 (11)
C(53)	10160 (5)	7936 (4)	10285 (4)	86 (14)
C(54)	10134 (5)	6710 (4)	10526 (4)	98 (17)
C(55)	8796 (5)	5802 (4)	10394 (4)	92 (16)
C(56)	7484 (5)	6119 (4)	10020 (4)	67 (11)
Fe	1339 (1)	7779 (1)	4409 (1)	57 (1)
N(60)	3158 (5)	7304 (4)	5669 (3)	48 (7)
C(61)	3505 (5)	7970 (4)	4825 (3)	63 (11)
C(62)	2469 (5)	7309 (4)	3686 (3)	79 (14)
C(63)	1482 (5)	6234 (4)	3826 (3)	70 (12)
C(64)	1908 (5)	6231 (4)	5051 (3)	59 (11)
C(71)	−623 (9)	7692 (7)	4357 (9)	102 (18)
C(72)	576 (9)	8720 (7)	5134 (9)	120 (20)
C(73)	1155 (9)	9499 (7)	4461 (9)	102 (18)
C(74)	314 (9)	8952 (7)	3268 (9)	95 (16)
C(75)	−785 (9)	7835 (7)	3204 (9)	77 (13)

Table 2. *Bond distances* (Å), *angles* (°) *and hydrogen-bond geometry* (Å, °) *with e.s.d.'s in parentheses*

(I)		(II)	
Co—N(1)	1.879 (3)	Co—N(1)	1.879 (8)
Co—N(2)	1.878 (3)	Co—N(2)	1.867 (6)
Co—N(3)	1.880 (3)	Co—N(3)	1.881 (6)
Co—N(4)	1.873 (3)	Co—N(4)	1.885 (8)
Co—C(5)	2.018 (5)	Co—C(5)	2.051 (7)
Co—N(60)	2.043 (3)	Co—N(60)	2.066 (3)
N(1)—C(1)	1.294 (6)	N(1)—C(1)	1.282 (11)
N(1)—O(11)	1.351 (5)	N(1)—O(11)	1.350 (9)
N(2)—C(2)	1.307 (6)	N(2)—C(2)	1.301 (13)
N(2)—O(22)	1.344 (5)	N(2)—O(22)	1.348 (9)
N(3)—C(3)	1.298 (5)	N(3)—C(3)	1.281 (12)
N(3)—O(33)	1.336 (4)	N(3)—O(33)	1.366 (9)
N(4)—C(4)	1.294 (5)	N(4)—C(4)	1.309 (10)
N(4)—O(44)	1.342 (5)	N(4)—O(44)	1.337 (9)
C(1)—C(2)	1.451 (7)	C(1)—C(2)	1.468 (13)
C(1)—C(11)	1.488 (8)	C(1)—C(11)	1.524 (17)
C(2)—C(22)	1.496 (7)	C(2)—C(22)	1.493 (12)
C(3)—C(4)	1.457 (6)	C(3)—C(4)	1.459 (12)
C(3)—C(33)	1.485 (7)	C(3)—C(33)	1.499 (12)
C(4)—C(44)	1.495 (8)	C(4)—C(44)	1.471 (17)
N(60)—C(61)	1.395 (5)	C(5)—C(51)	1.473 (11)
N(60)—C(64)	1.396 (5)	C(51)—C(52)	1.395 (6)
C(61)—C(62)	1.386 (7)	C(51)—C(56)	1.395 (7)
C(62)—C(63)	1.394 (8)	C(52)—C(53)	1.395 (8)
C(63)—C(64)	1.391 (6)	C(53)—C(54)	1.395 (7)
Fe—N(60)	2.046 (3)	C(54)—C(55)	1.395 (6)
Fe—C(61)	2.027 (5)	C(55)—C(56)	1.395 (8)
Fe—C(62)	2.046 (5)	N(60)—C(61)	1.390 (6)
Fe—C(63)	2.046 (5)	N(60)—C(64)	1.390 (5)
Fe—C(64)	2.027 (4)	C(61)—C(62)	1.390 (4)
C(71)—C(72)	1.359 (9)	C(62)—C(63)	1.390 (6)
C(71)—C(75)	1.348 (9)	C(630—C(64)	1.390 (5)
C(72)—C(73)	1.357 (11)	Fe—N(60)	2.020 (5)
C(73)—C(74)	1.404 (15)	Fe—C(61)	2.028 (6)
C(74)—C(75)	1.363 (14)	Fe—C(62)	2.037 (5)
Fe—C(71)	2.044 (5)	Fe—C(63)	2.035 (5)
Fe—C(72)	2.037 (7)	Fe—C(64)	2.035 (4)
Fe—C(73)	2.013 (6)	C(71)—C(72)	1.390 (9)
Fe—C(74)	2.011 (11)	C(71)—C(75)	1.390 (16)
Fe—C(75)	2.031 (8)	C(72)—C(73)	1.390 (15)
		C(73)—C(74)	1.390 (13)
		C(74)—C(75)	1.390 (11)
		Fe—C(71)	2.021 (11)
		Fe—C(72)	2.025 (10)
		Fe—C(73)	2.034 (9)
		Fe—C(74)	2.036 (9)
		Fe—C(75)	2.029 (10)

N(1)—Co—N(2)	81.0 (1)	N(1)—Co—N(2)	81.4 (3)
N(1)—Co—N(3)	98.2 (1)	N(1)—Co—N(3)	99.5 (3)
N(1)—Co—N(4)	176.8 (1)	N(1)—Co—N(4)	178.4 (3)
N(1)—Co—C(5)	89.6 (2)	N(1)—Co—C(5)	85.3 (3)
N(1)—Co—N(60)	94.0 (1)	N(1)—Co—N(60)	93.4 (2)
N(2)—Co—N(3)	176.4 (1)	N(2)—Co—N(3)	177.3 (3)
N(2)—Co—N(4)	98.7 (1)	N(2)—Co—N(4)	97.9 (3)
N(2)—Co—C(5)	88.4 (2)	N(2)—Co—C(5)	90.6 (3)
N(2)—Co—N(60)	93.1 (1)	N(2)—Co—N(60)	93.2 (2)
N(3)—Co—N(4)	81.8 (1)	N(3)—Co—N(4)	81.1 (3)
N(3)—Co—C(5)	88.0 (2)	N(3)—Co—C(5)	87.0 (3)
N(3)—Co—N(60)	90.4 (1)	N(3)—Co—N(60)	93.2 (2)
N(4)—Co—C(5)	87.3 (2)	N(4)—Co—C(5)	93.2 (3)
N(4)—Co—N(60)	89.1 (1)	N(4)—Co—N(60)	88.2 (2)
C(5)—Co—N(60)	176.2 (2)	C(5)—Co—N(60)	175.8 (3)
Co—N(1)—C(1)	117.7 (3)	C(50—N(1)—C(1)	116.7 (6)
Co—N(1)—O(11)	123.0 (2)	Co—N(1)—O(11)	122.6 (5)
C(1)—N(1)—O(11)	119.3 (3)	C(1)—N(1)—O(11)	120.7 (7)
Co—N(2)—C(2)	116.5 (3)	Co—N(2)—C(2)	117.5 (6)
Co—N(2)—O(22)	122.6 (3)	Co—N(2)—(22)	123.8 (5)
C(2)—N(2)—O(22)	120.9 (4)	C(20—N(2)—O(22)	118.8 (7)
Co—N(3)—C(3)	115.9 (3)	Co—N(3)—C(3)	117.0 (5)
Co—N(3)—O(33)	122.6 (2)	Co—N(3)—O(33)	121.7 (5)
C(3)—N(3)—O(33)	121.4 (3)	C(3)—N(3)—O(33)	121.3 (7)
Co—N(4)—C(4)	116.9 (3)	Co—N(4)—C(4)	116.9 (5)
		Co—N(4)—O(44)	122.9 (5)
Co—N(4)—C(44)	122.7 (3)	C(4)—N(4)—O(44)	120.2 (7)
C(4)—N(4)—O(44)	120.4 (3)	N(1)—C(1)—C(2)	113.1 (8)
N(1)—C(1)—C(2)	111.8 (4)	N(1)—C(1)—C(11)	124.5 (8)
N(1)—C(1)—C(11)	124.7 (4)	C(2)—C(1)—C(11)	122.4 (8)
C(2)—C(1)—C(11)	123.5 (4)	N(2)—C(2)—C(1)	111.2 (7)
N(2)—C(2)—C(1)	112.9 (4)	N(2)—C(2)—C(22)	123.8 (8)
N(2)—C(2)—C(22)	123.1 (5)	C(1)—C(2)—C(22)	125.0 (8)
C(1)—C(2)—C(22)	124.0 (5)	N(3)—C(3)—C(4)	113.5 (7)
N(3)—C(3)—C(4)	113.1 (4)	N(3)—C(3)—C(33)	123.3 (8)
N(3)—C(3)—C(33)	122.4 (4)	C(4)—C(3)—C(33)	123.0 (8)

attributed to O(11) or O(33) [O(11)···H = 1.28 (8) Å, O(33)···H = 1.24 (8) Å], suggesting a D_{2h} local symmetry distribution.

The Co—N(ax.) distance is 2.043 (3) in (I) and 2.066 (3) Å in (II). If we compare a series of methylcobaloximes, it can be seen that the Co—N(ax.) distance in (I) is shorter than those measured in

Table 2. (*cont.*)

(I)		(II)	
C(4)—C(3)—C(33)	124.4 (4)	N(4)—C(4)—C(3)	111.4 (7)
N(4)—C(4)—C(3)	112.3 (4)	N(4)—C(4)—C(44)	122.3 (8)
N(4)—C(4)—C(44)	123.3 (4)	C(3)—C(4)—C(44)	126.2 (8)
C(3)—C(4)—C(44)	124.4 (4)	Co—C(5)—C(51)	117.8 (5)
C(61)—N(60)—C(64)	105.5 (3)	C(5)—C(51)—C(52)	120.5 (5)
N(60)—C(61)—C(62)	110.0 (4)	C(5)—C(51)—C(56)	119.5 (5)
C(61)—C(62)—C(63)	107.4 (4)	C(52)—C(51)—C(56)	120.0 (5)
C(62)—C(63)—C(64)	107.2 (4)	C(51)—C(52)—C(53)	120.0 (5)
N(60)—C(64)—C(63)	106.9 (4)	C(52)—C(53)—C(54)	120.0 (4)
C(72)—C(71)—C(75)	108.1 (6)	C(53)—C(54)—C(55)	120.0 (5)
C(71)—C(72)—C(72)	108.5 (6)	C(54)—C(55)—C(56)	120.0 (5)
C(72)—C(73)—C(74)	107.8 (8)	C(51)—C(56)—C(55)	120.0 (4)
C(73)—C(74)—C(75)	105.8 (9)	C(61)—N(60)—C(64)	108.0 (3)
C(71)—C(75)—C(74)	109.8 (8)	N(60)—C(61)—C(62)	108.0 (3)
		C(61)—C(62)—C(63)	108.0 (4)
		C(62)—C(63)—C(64)	108.0 (3)
		N(60)—C(64)—C(63)	108.0 (4)
		C(72)—C(71)—C(75)	108.0 (8)
		C(71)—C(72)—C(73)	108.0 (9)
		C(72)—C(73)—C(74)	108.0 (7)
		C(73)—C(74)—C(75)	108.0 (9)
		C(71)—C(75)—C(74)	108.0 (7)

	O—H	H···O	O···O	O—H···O
(I)	1.18 (5)	1.32 (5)	2.470 (5)	164 (1)
	1.23 (5)	1.27 (5)	2.473 (3)	163 (1)
(II)	1.28 (8)	1.24 (8)	2.486 (7)	161 (2)
	1.15 (8)	1.32 (8)	2.472 (7)	173 (2)

methyl(Co)$(DH)_2$(methylimidazole), 2.058 (5) Å, or methyl(Co)$(DH)_2$(pyridine), 2.068 (3) Å (Bigotto, Zangrando & Randaccio, 1976). In this case, therefore, AF coordinates tightly to the Co^{III} center. In contrast, benzyl compound (II) exhibits a Co—N(ax.) distance slightly longer than that reported in benzyl(Co)$(DH)_2$(pyridine), 2.056 (3) Å (Bresciani Pahor, Randaccio, Zangrando & Antolini, 1988). For alkylcobaloximes studied up to now the Co—*L*(ax.) distance increased with the σ-donor power of the *trans*-alkyl group (Randaccio, Bresciani Pahor, Zangrando & Marzilli, 1989). The opposite effect observed for (I) and (II) could be explained assuming that the azaferrocene ligand displays not only σ-donor but also considerable π-acceptor properties. In such a case, a stronger σ-donor ligand (methyl) increasing the electron density at Co would bring about stronger metal-to-nitrogen back bonding and consequently shorten the Co—N(ax.) distance.

The Co—C bond length is less affected by the nature of the N-donor ligand. This is confirmed by a comparison of methyl derivatives of different ligands whose values are identical within experimental error: 2.018 (5) Å for L = azaferrocene, 2.009 (7) Å for L = methylimidazole and 1.998 (5) Å for L = pyridine (Bigotto, Zangrando & Randaccio, 1976). Otherwise it is known that the Co—C distance is mainly influenced by the bulk of the alkyl group and may increase for a given ligand by 0.15 Å, going from a methyl to an adamentyl derivative (Bigotto, Zangrando & Randaccio, 1976; Bresciani Pahor, Marzilli, Randaccio, Toscano & Zangrando, 1984). Similar behaviour is observed in the two AF complexes with a lengthening of 0.03 Å for the benzyl derivative. The φ—CH_2—Co angle is slightly distorted 117.8 (5)°. This distortion is too weak to minimize the steric repulsion between the π ligand and the equatorial N donors, so the Co—C distance should lengthen.

The axially coordinated ligand azaferrocene exhibits a typical sandwich structure, the η^5-cyclopentadienyl rings being planar and roughly parallel [3.5° for (I) and 4.0° for (II), the N atom being further away from the cyclopentadienyl]. The two rings of the azaferrocene system are nearly eclipsed in (II) (rotation of the two five-membered rings is 8°) and more staggered in (I) (20°). The η^5-pyrrolyl ligand plane makes an angle of 108° for (I) and 109° for (II) with the coordination plane; these results differ from those usually found (about 90°) in cobaloximes containing heterocyclic N bases, and are

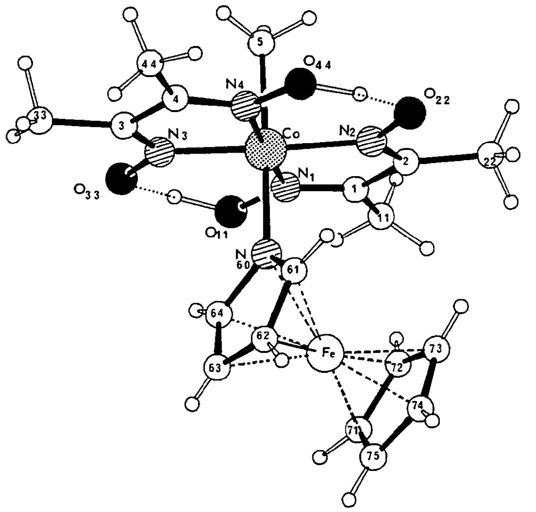

Fig. 1. A perspective view of methyl(η^1-azaferrocene)cobaloxime. (Disorder is not shown for clarity.)

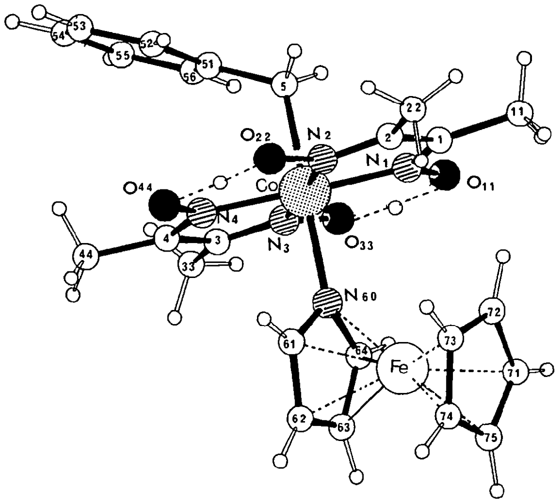

Fig. 2. A perspective view of benzyl(η^1-azaferrocene)cobaloxime.

probably a result of steric interactions between the AF ligand and the macrocycle. Benzyl and azaferrocene ligands coordinated to the upper and lower site are centrosymmetrically located on each side of the macrocycle (Fig. 2), so that steric interactions between benzyl and one DH unit, and AF and the other one, could be equally spread.

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Two Different (Croconato)(2,2′:6′,2″-terpyridyl)copper(II) Complexes in One Single Crystal: Structure of $[Cu(C_{15}H_{11}N_3)(H_2O)(C_5O_5)][Cu(C_{15}H_{11}N_3)(C_5O_5)].4H_2O$

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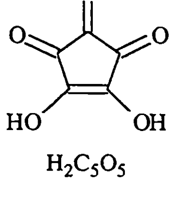
Abstract. $[Cu(C_{15}H_{11}N_3)(C_5O_5)(H_2O)][Cu(C_{15}H_{11}N_3)(C_5O_5)].4H_2O$, $M_r = 963.8$, triclinic, $P\bar{1}$, $a = 15.204$ (3), $b = 12.825$ (2), $c = 11.006$ (2) Å, $\alpha = 84.18$ (2), $\beta = 110.18$ (2), $\gamma = 105.22$ (2)°, $V = 1944$ (1) Å^3, $Z = 2$, $D_x = 1.646$ Mg m^{-3}, $F(000) = 984$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 1.17$ mm^{-1}, $T = 288$ K, final $R = 0.062$ and $wR = 0.070$ for 3664 observed reflections. The crystal structure consists of two neutral mononuclear copper(II) entities of formula $[Cu(terpy)(C_5O_5)]$ (1) and $[Cu(terpy)(C_5O_5)(H_2O)]$ (2) and four uncoordinated water molecules. The coordination of the copper(II) ion in (1) may be viewed as a square-based pyramid with the three N atoms of the 2,2′:6′,2″-terpyridine and an O atom of the croconate building the basal plane, whereas another O atom of the croconate occupies the apical site. In (2), 2,2′:6′,2″-terpyridine and croconate act also as terdentate and bidentate ligands, respectively, but a water molecule occupies the sixth position leading to a distorted octahedral environment.

Introduction. The cyclic oxocarbon dianions, $C_nO_n^{2-}$ (deltate, squarate, croconate and rhodizonate, for $n = 3$, 4, 5 and 6, respectively) have been recognized as a family of unusually stable species with electron



$H_2C_5O_5$

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