Fig. 2. An *ORTEP*II (Johnson, 1976) projection perpendicular to the *bc* plane showing the contents of one unit cell, with a unit cell outlined. The *c* axis is horizontal. Au and Br atoms are shown shaded; H atoms are not shown.

are close to linear [172.0 (1) and 175.5 (1)°], appropriate for the + 1 oxidation state of the Au. All four cyclohexyl rings are in the chair conformation, with average C—C distance of 1.517 (11) Å and average C—C—C angle of 111.5 [11]°.

The molecules pack in the crystal more or less extended in the *z* direction. There are a few contacts shorter than van der Waals distances; the two shortest (3.10, 3.23 Å) involve cyclohexyl C atoms and N atoms of the cyanide groups, so they are not present in all unit cells. All other intermolecular distances are greater than 3.7 Å.

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Structure of *trans*-Bis[dimethylglyoximato(1 −)-*N*,*N'*]bis(pyridine-*N*)cobalt(III) Tetrachloroferrate(III)

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Abstract. [Co($C_4H_7N_2O_2$)$_2$(C_5H_5N)$_2$][FeCl$_4$], M_r = 645.1, triclinic, $P\bar{1}$, a = 9.306 (3), b = 16.247 (3), c = 8.972 (2) Å, α = 104.72 (2), β = 96.38 (2), γ = 80.44 (2)°, V = 1290.4 (7) Å^3, Z = 2, D_m = 1.67, D_x = 1.660 g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ = 16.93 cm^{-1}, $F(000)$ = 654, room temperature, R = 0.062 for 4566 observed reflections. The crystal consists of cobaloxime cations and FeCl$_4^-$ anions. Two crystallographically independent cobaloxime cations occupy the individual centres of symmetry. The cobaloxime cations exhibit a distorted octahedral coordination with the four oxime N donors at the equatorial positions and two pyridyl N donors at the axial sites. The tetrahedral FeCl$_4^-$ anion is stabilized by the large cobaloxime cation in the crystal.

Introduction. Recently the complexes of LCo(DH)$_2R$, where L = neutral amine ligand, R = alkyl group and DH = monoanion of dimethylglyoxime, have been extensively studied as a simple molecular model of the vitamin B$_{12}$ system (Bresciani Pahor, Forcolin, Randaccio, Marzilli, Summers & Toscano, 1985).

From the viewpoint of biomimic transition-metal chemistry, the biochemical steps of greatest interest when considering B_{12} are the Co—C(R) bond-cleavage step and the rearrangement reaction of the substrate (Finke, Schiraldi & Mayer, 1984; Toscano & Marzilli, 1984). It has been revealed that the axial Co—C(R) bond strength is reflected in the distance of the Co—N(L) bond located on the opposite axial position, i.e. trans influence. In order to reveal the quantitative relationship between Co—C bond strength and Co—N distance, a number of cobaloximes have been investigated. The structure of the title complex, in which both axial ligands are pyridine, is presented here to compare the trans influence of the alkyl groups with that of the pyridine ligand.

Experimental. A crystal, $0.30 \times 0.18 \times 0.12$ mm, was obtained from methanol solution. D_m was measured by flotation. An Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation was used for data collection: ω–2θ scan technique, scan width $\Delta\omega = (0.80 + 0.35\tan\theta)°$, scan rate variable at 0.8–$5.5°$ min^{-1}. Unit-cell parameters were determined by least-squares fit of 25 reflections with $25 \le 2\theta \le 35°$. Three standard reflections determined every hour showed no significant intensity variation. A total of 5487 independent reflections were measured in the range $2 \le 2\theta \le 54°$, $h = -11$ to 11, $k = 0$ to 20 and $l = -11$ to 11; 4566 reflections with $|F_o| \ge 3\sigma(F_o)$ were used for structure determination. Lp corrections were applied, but no absorption or extinction corrections were used.

In the unit cell the Fe^{III} atom is located at a general position while two independent Co^{III} atoms are located at the special positions $(0,0,0)$ and $(0,0.5,0)$ (see Fig. 1); therefore, a pseudo-centre of inversion appeared at $(0,0.25,0)$ on the Patterson map. To solve the structure, a combination of Patterson function, trial-and-error methods and direct methods (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) was used. The structure was refined by block-diagonal least squares using *HBLS*-V (Ashida, 1979), minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ with unit weights. H atoms were found on a difference Fourier map. Refinement with anisotropic thermal parameters for non-H atoms and with isotropic thermal parameters for H atoms reduced R to 0.062 and wR to 0.094 with $S = 6.61$ and $(\Delta/\sigma)_{max} = 0.20$ for non-H atoms. On the final difference Fourier map $\Delta\rho_{max} = 1.2$ and $\Delta\rho_{min} = -0.7$ e Å^{-3} within 1.0 Å from the Co^{III} atoms. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All computations were performed on a Honeywell DPS8/49 computer at The Computation Centre of Zhejiang University.

Discussion. The atomic coordinates and equivalent isotropic temperature factors of non-H atoms are listed in Table 1.* Selected bond distances and angles are presented in Table 2. The crystal structure consists of cobaloxime cations and tetrachloroferrate anions. In the cell, two anions are related by an inversion centre, whereas two crystallographically independent cobaloxime cations are located about the individual inversion centres (Fig. 1). As shown in
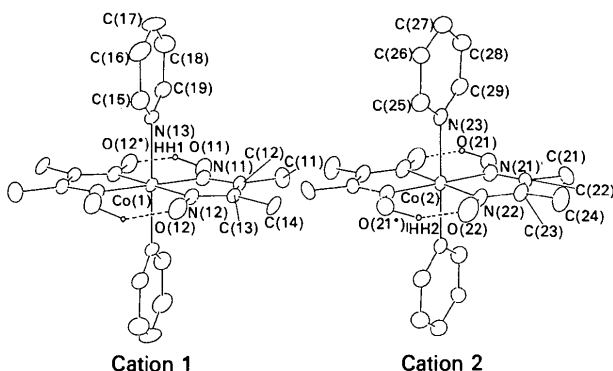
Fig. 1. Structures of the title cations together with the atomic numbering system. H atoms, except oxime H atoms, are omitted for clarity.
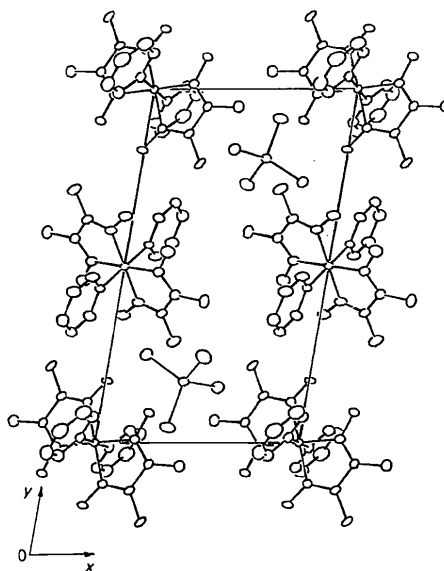

Fig. 2. Crystal structure of the title compound projected along the c^* axis. H atoms are omitted for clarity.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *of non-H atoms with e.s.d.'s in parentheses*

B_{eq} is defined by Hamilton (1959).

	x	y	z	B_{eq}
Co(1)	0.0	0.0	0.0	1.90
Co(2)	0.0	0.5	0.0	2.15
Fe	0.4153 (1)	0.23847 (8)	0.4189 (2)	2.87
Cl(1)	0.5721 (3)	0.1936 (2)	0.2374 (3)	4.26
Cl(2)	0.5041 (4)	0.3339 (2)	0.6070 (4)	5.62
Cl(3)	0.2079 (3)	0.2985 (2)	0.3252 (3)	4.46
Cl(4)	0.3813 (4)	0.1297 (2)	0.5075 (3)	4.73
N(11)	0.1962 (7)	0.0195 (4)	0.0562 (8)	2.6
N(12)	0.0758 (7)	−0.1066 (4)	0.0527 (8)	2.5
N(13)	−0.0503 (7)	0.0514 (4)	0.2162 (8)	2.6
N(21)	0.1803 (8)	0.4995 (4)	0.1167 (9)	3.4
N(22)	0.0854 (8)	0.3857 (4)	−0.0934 (8)	3.1
N(23)	−0.0835 (7)	0.4582 (4)	0.1583 (8)	2.7
O(11)	0.2435 (7)	0.0937 (4)	0.0535 (8)	3.4
O(12)	−0.0046 (7)	−0.1684 (4)	0.0379 (8)	3.3
O(21)	0.2190 (8)	0.5687 (4)	0.2227 (8)	5.0
O(22)	0.0137 (7)	0.3338 (4)	−0.2027 (7)	3.5
C(11)	0.4400 (10)	−0.0370 (6)	0.1555 (12)	3.9
C(12)	0.2854 (8)	−0.0411 (5)	0.1005 (9)	2.5
C(13)	0.2149 (9)	−0.1166 (5)	0.0948 (9)	2.5
C(14)	0.2957 (10)	−0.1962 (6)	0.1356 (11)	3.3
C(15)	−0.1342 (11)	0.0150 (6)	0.2842 (11)	3.7
C(16)	−0.1721 (13)	0.0506 (8)	0.4356 (13)	4.9
C(17)	−0.1141 (15)	0.1222 (8)	0.5181 (12)	5.3
C(18)	−0.0271 (14)	0.1596 (7)	0.4482 (13)	5.1
C(19)	0.0024 (10)	0.1222 (6)	0.2964 (11)	3.5
C(21)	0.4281 (11)	0.4208 (8)	0.1500 (16)	5.4
C(22)	0.2753 (9)	0.4295 (6)	0.0798 (11)	3.5
C(23)	0.2147 (10)	0.3617 (5)	−0.0388 (10)	3.0
C(24)	0.2933 (12)	0.2734 (7)	−0.0943 (13)	4.4
C(25)	−0.1144 (11)	0.3769 (6)	0.1246 (11)	3.6
C(26)	−0.1758 (10)	0.3470 (6)	0.2308 (12)	3.6
C(27)	−0.2088 (11)	0.3999 (7)	0.3727 (12)	4.1
C(28)	−0.1748 (13)	0.4821 (7)	0.4057 (12)	4.3
C(29)	−0.1124 (12)	0.5090 (6)	0.2991 (11)	3.8

Table 2. *Selected bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Co(1)—N(11)	1.896 (7)		Co(1)—N(12)	1.912 (7)
Co(1)—N(13)	1.982 (7)		Co(2)—N(21)	1.876 (8)
Co(2)—N(22)	1.911 (8)		Co(2)—N(23)	1.999 (7)
N(11)—O(11)	1.357 (10)		N(12)—O(12)	1.321 (10)
N(21)—O(21)	1.346 (11)		N(22)—O(22)	1.318 (10)
N(11)—C(12)	1.292 (11)		N(12)—C(13)	1.303 (11)
N(13)—C(15)	1.333 (12)		N(13)—C(19)	1.330 (12)
N(21)—C(22)	1.314 (13)		N(22)—C(23)	1.285 (12)
N(23)—C(25)	1.350 (12)		N(23)—C(29)	1.348 (13)
C(11)—C(12)	1.475 (13)		C(12)—C(13)	1.471 (11)
C(13)—C(14)	1.493 (12)		C(21)—C(22)	1.489 (17)
C(22)—C(23)	1.463 (14)		C(23)—C(24)	1.487 (15)
Fe—Cl(1)	2.210 (3)		Fe—Cl(2)	2.173 (4)
Fe—Cl(3)	2.194 (3)		Fe—Cl(4)	2.193 (3)
O(11)—HH1	1.07 (14)		O(12*)—HH1	1.47 (14)
O(21*)—HH2	1.35 (14)		O(22)—HH2	1.14 (14)

N(11)—Co(1)—N(12)	81.4 (3)		N(11)—Co(1)—N(13)	90.2 (3)
N(12)—Co(1)—N(13)	90.0 (3)		N(21)—Co(2)—N(22)	81.9 (3)
N(21)—Co(2)—N(23)	90.2 (3)		N(22)—Co(2)—N(23)	89.0 (3)
Co(1)—N(11)—O(11)	122.7 (5)		Co(1)—N(12)—O(12)	122.5 (5)
Co(1)—N(11)—C(12)	117.1 (6)		Co(1)—N(12)—C(13)	115.4 (6)
Co(2)—N(21)—O(21)	123.3 (6)		Co(2)—N(22)—O(22)	121.9 (6)
Co(2)—N(21)—C(22)	116.2 (7)		Co(2)—N(22)—C(23)	115.7 (7)
Co(1)—N(13)—C(15)	120.9 (6)		Co(1)—N(13)—C(19)	120.0 (6)
Co(2)—N(23)—C(25)	119.7 (6)		Co(2)—N(23)—C(29)	122.0 (7)
O(11)—N(11)—C(12)	120.2 (2)		O(12)—N(12)—C(13)	121.9 (7)
O(21)—N(21)—C(22)	120.1 (8)		O(22)—N(22)—C(23)	122.3 (8)
N(11)—C(12)—C(11)	125.5 (8)		N(11)—C(12)—C(13)	112.4 (7)
C(11)—C(12)—C(13)	122.1 (8)		N(12)—C(13)—C(12)	113.5 (7)
N(12)—C(13)—C(14)	123.7 (8)		C(12)—C(13)—C(14)	122.8 (7)
N(21)—C(22)—C(21)	123.6 (10)		N(21)—C(22)—C(23)	112.5 (9)
C(21)—C(22)—C(23)	124.0 (10)		N(22)—C(23)—C(22)	113.5 (8)
N(22)—C(23)—C(24)	122.2 (9)		C(22)—C(23)—C(24)	124.3 (9)
C(15)—N(13)—C(19)	119.1 (8)		C(25)—N(23)—C(29)	118.3 (8)
Cl(1)—Fe—Cl(2)	109.0 (1)		Cl(1)—Fe—Cl(3)	109.9 (1)
Cl(1)—Fe—Cl(4)	109.6 (1)		Cl(2)—Fe—Cl(3)	108.5 (1)
Cl(2)—Fe—Cl(4)	109.0 (1)		Cl(3)—Fe—Cl(4)	110.7 (1)

Fig. 2, both cations 1 and 2 have the same configuration as that reported previously, that is, a distorted octahedral coordination with four oxime N donors at the equatorial positions and two pyridyl N donors at the axial sites. The bond distances and angles of the $Co(DH)_2$ moieties in the present complex are in agreement with those found for most $LCo(DH)_2R$ complexes (Bresciani Pahor, Forcolin, Randaccio, Marzilli, Summers & Toscano, 1985). The average equatorial Co—N distance of 1.899 Å is about 0.02 Å longer than the average distance of 1.880 Å observed in two cobaloxime molecules, each containing a pyridine ligand at the axial site, reported by Bresciani Pahor, Randaccio, Zangrando & Antolini (1988). As the Co^{III} atoms occupy the inversion centre, the four oxime N donors are strictly coplanar with the Co^{III} atom, while each DH unit is planar within ± 0.09 Å. There are intramolecular hydrogen bonds in both cations, O(11)···O(12*) = 2.509 (10), O(21*)···O(22) = 2.480 (10) Å. In the axial direction of cation 1, the pyridine ring, planar within ± 0.02 Å, is perpendicular to the equatorial plane and bisecting the oxime H bridge. The Co—N(py) distance of 1.982 (7) Å is significantly shorter than the average distance of 2.056 Å for complexes of the type $pyCo(DH)_2R$ (Bresciani Pahor, Forcolin, Randaccio, Marzilli, Summers & Toscano, 1985) but is slightly longer than the value of 1.973 Å found in the $pyCo(DH)_2N_3$ complex (Clearfield, Gopal, Kline, Sipski & Urban, 1978; Ponnuswamy & Trotter, 1983). Whereas the axial Co—N(py) distance of 1.999 (7) Å in cation 2 is close to the shortest Co—N distance reported hitherto for complexes of the type $pyCo(DH)_2R$ (Bresciani Pahor, Randaccio, Zangrando & Antolini, 1988). The lengthening of the Co—N(py) distance in cation 2 might be a result of steric repulsion between the pyridine and oxime ligands, as evidenced by the N(22)···C(25) distance of 2.88 (1) Å and the N(22)···C(29) distance of 2.87 (1) Å. In turn, this repulsion seems to be the result of deflection of the pyridine plane towards the N(22) atom, which might be caused by the short contact between the pyridine and $FeCl_4^-$ anion [Cl(3)···C(25) = 3.54 (1) Å]. This result suggests that both the steric and the electronic effects affect the Co—N(py) distance. The Co—N(py) distances of both cation 1 and 2 are in contrast with those distances (1.946 and 1.954 Å) reported by Ablov, Dvolkin, Simonov, Bologa & Malinovskii (1974).

It has been shown previously that FeX_4^- ions (X = halogen) can be stabilized by very large cations (Wells, 1975): the $FeCl_4^-$ anion is stable in the present crystal. The coordination geometry around the Fe^{III} atom is tetrahedral, and the Fe—Cl distances of 2.174 (4)–2.211 (3) Å are slightly longer than the 2.162 (5) Å reported previously (Bennett, Cotton & Weaver, 1967).

The crystal structure projected along the c^* axis is illustrated in Fig. 1. The shortest distance between the anion and the cation is 3.54 (1) Å between atoms Cl(3) and C(25). The spatial orientation of the two independent cations is different; the dihedral angle between the coordination planes of cations 1 and 2 is 46.8°.

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Structure of Tris(dimethylglyoxime)ruthenium(II) Dichloride

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Abstract. (I) [Ru(C₄H₈N₂O₂)₃]Cl₂, $M_r = 520$, monoclinic, $C2/c$, $a = 13.4890$ (5), $b = 9.6913$ (7), $c = 16.6847$ (5) Å, $\beta = 112.365$ (3)°, $V = 2017$ (2) Å³, $Z = 4$, $D_x = 1.71$ g cm⁻³, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 93.2$ cm⁻¹, $F(000) = 1056$, $T = 295$ (2) K, final $R = 0.048$ ($wR = 0.053$) for 1623 significant [$|F_{obs}| \geq 3\sigma(|F_{obs}|)$] reflections. The molecule is propeller-like with three dimethylglyoxime-H₂ (dmgH₂) units bound to the Ru^II ion and occupies a special position (on a crystallographic twofold axis) in the unit cell. The Ru^II coordination is a distorted octahedron, Ru^II—N bonds [average 2.038 (4) Å] are even shorter than typical Ru^III—N distances (2.10 Å), implying considerable π bonding between the π^* orbitals of dmg and the t_{2g} orbitals of Ru^II; the N—Ru—N bite angle (average) is 75.0 (2)°. The crystal structure is stabilized by intermolecular H bonding of the type O—H⋯Cl only and not by the intramolecular O—H⋯O interactions commonly observed in *trans*-bis(dmg) complexes.

Introduction. Although there is a wealth of literature available on *trans*-bis(dimethylglyoximato)metal complexes (Chakravorty, 1974; Mariassy & Ondrejovic, 1990; Konno, Okamoto & Shirotani, 1989; Koman, Mariassy & Ondrejovic, 1991) along with a few *cis* isomers (Dwyer & Nyholm, 1946; Gillard & Wilkinson, 1963; Alcock, Atkins, Curzon, Golding & Sellars, 1980; Alcock, Atkins, Golding & Sellars, 1982), the tris(dimethylglyoxime)metal complexes are reported infrequently (Nakahara, Fujita & Tsuchida, 1956; Burger, Ruff & Ruff, 1965) and not characterized fully. A related example, whose X-ray structure is also reported, is the tris(oxamide oxime)-cobalt(III) complex (Bekaroglu, Sarisaban, Koray, Nuber, Weidenhammer, Weiss & Ziegler, 1978). This paper presents the first crystal structure of a tris-(dimethylglyoxime) complex with ruthenium(II). Studies on ruthenium(II) complexes like the title compound (I) are carried out in our laboratory with the aim of understanding the underlying chemical and structural features responsible for the excited-state phenomena exhibited by these molecules, for example the tris(2,2'-bipyridyl)ruthenium(II) complex, a well known model compound for the photodissociation of water into oxygen and hydrogen (Rillema, Jones & Levy, 1979).