However, in *W*(1) one of its lone pairs is directed to Na^+ and the other to a H of a different water molecule. O(1), O(4) and O(6), which are at distances of 1·266, 1·272 and 1·271 Å from their respective C atoms, accept hydrogens of water molecules and take part in hydrogen-bond formation. The other O atoms whose bonding involves more double-bond character, as judged by their shorter C–O distances, are not involved in hydrogen-bond formation. Na(1) and Na(2) are coordinated by four carboxylate O atoms and two water molecules (see Fig. 1); Na(3) and Na(4) are coordinated by five carboxylate O atoms and one water molecule. The malonate dianions form four- and six-membered chelate rings with the different Na^+ ions. Similar sixfold coordination of Na is found in salts of other carboxylic and dicarboxylic acids (Speakman & Mills, 1961; Narasinga Rao & Parthasarathy, 1974).

Fig. 2 shows the approximately tetrahedral coordination of both the crystallographically distinct Li^+ ions in Li_2mal, made up by four O atoms. The malonate dianion forms a six-membered chelate ring with Li(1).

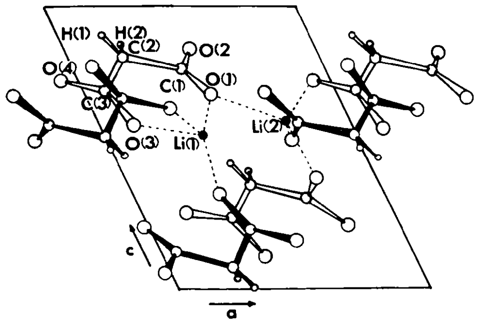

Fig. 2. The crystal structure of dilithium malonate, seen in its *b* axial projection.

Fourfold coordination of Li had been found in salts of other carboxylic and dicarboxylic acids (Soriano-Garcia & Parthasarathy, 1978; Gonschorek & Küppers, 1975).

We wish to thank Dr R. Parthasarathy for his keen interest in this work and for many helpful discussions. Modified versions of the following programs were used: *BDL*-6 (Gantzel, Sparks & Trueblood, ACA old program No. 317) and *ORTEP* (Johnson, 1965). Fourier and torsion-angle programs were written by Dr S. T. Rao.

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Bis{3-[2-(2-pyridyl)ethyl]imino-2-butanone oximato}cobalt(III) Perchlorate, $C_{22}H_{28}CoN_6O_2^+.ClO_4^-$

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Abstract. $M_r = 566{\cdot}89$, triclinic, $P\bar{1}$, $a = 8{\cdot}803\ (4)$, $b = 11{\cdot}785\ (6)$, $c = 13{\cdot}333\ (7)$ Å, $\alpha = 95{\cdot}55\ (4)$, $\beta = 91{\cdot}58\ (4)$, $\gamma = 111{\cdot}79\ (3)°$, $V = 1275\ (1)$ Å^3, $Z = 2$, $D_m = 1{\cdot}48\ (2)$, $D_x = 1{\cdot}476$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}86$ mm^{-1}, $F(000) = 588$, $T = 298$K, $R = 0{\cdot}043$ for 3964 observed reflections. The structure comprises $[Co(C_{11}H_{14}N_3O)_2]^+$ cations and ClO_4^- anions. Co is coordinated to six N atoms of the two tridentate ligand molecules in the form of a slightly distorted octahedron.

Introduction. Though metal complexes of tridentate 3-[2-(2-pyridyl)ethyl]imino-2-butanone oxime have been investigated fairly thoroughly (Uhling & Schneider,

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1964; Uhling, Schneider & Hildebrandt, 1966), the crystal structure has been reported only for the Cu^{II} complex (Bertrand, Smith & VanDerveer, 1977). The ligand forms complexes with transition metals in both neutral and deprotonated form. With Co^{II} salts and atmospheric oxygen as oxidant, the ligand reacts in deprotonated form giving Co^{III} complexes. The title compound whose crystal structure is discussed here is a representative of such complexes.

Experimental. Prepared by the method of Uhling *et al.* (1966), red crystals, recrystallized from ethanol, 0·3 × 0·3 × 0·4 mm crystal, Syntex $P2_1$ diffractometer, cell dimensions obtained from least-squares refinement of the angular settings of 15 reflections, intensity data measured by ω -scan technique, variable scan speed, 4803 independent reflections with $3 < 2\theta < 50°$, 3964 considered observed, $I > 2{\cdot}0\,\sigma(I)$, where $\sigma(I)$ was determined from counting statistics; periodically measured reference reflection showed only random variation and no systematic decay, intensities corrected for Lorentz and polarization effects but not for absorption. Combination of heavy-atom and Fourier-synthesis methods, full-matrix least-squares refinement minimizing $\sum w(|F_o|-|F_c|)^2$, $w = (10{\cdot}0 + |F_o| + 0{\cdot}0167|F_o|^2 + 0{\cdot}0003|F_o|^3)^{-1}$, scattering factors for non-H atoms from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965), Co values corrected for anomalous scattering (*International Tables for X-ray Crystallography,* 1974), all non-H atoms readily located; anisotropic refinement of positions gave $R = 0{\cdot}057$; although most of the H atoms of the ligands found in difference map, their positions were calculated geometrically (C—H = 1·00 Å) and included in subsequent refinement at fixed positions with fixed $U = 0{\cdot}06$ Å^2; in final least-squares cycle the average ratio of shift to error was 0·18, maximum value 0·67 for the U_{22} temperature factor of Co, final $R = 0{\cdot}043$, $R_w = 0{\cdot}071$, $S = 0{\cdot}79$, final difference map featureless, maximum peak 0·33 e Å^{-3}, Univac 1108 computer, XRAY system (Stewart, 1976).*

Discussion. The atomic coordinates, bond lengths and bond angles are listed in Tables 1 and 2.

Table 1. *Fractional atomic coordinates* (×10^4) *and* $U_{\rm eq}$ (×10^2) *for the nonhydrogen atoms*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$ (Å^2)
Co	1186·6 (6)	3041·3 (4)	2495·0 (4)	3·20 (3)
Cl	3504 (2)	2035 (1)	7448 (1)	6·9 (1)
O(1)	−1296 (4)	2867 (3)	1031 (2)	5·2 (2)
O(2)	373 (4)	4421 (3)	4082 (2)	5·8 (2)
O(3)	2032 (7)	1628 (5)	6808 (4)	11·2 (4)
O(4)	3507 (7)	1051 (4)	7975 (4)	10·3 (4)
O(5)	4846 (7)	2417 (5)	6834 (4)	11·0 (4)
O(6)	3569 (8)	3059 (4)	8151 (3)	12·0 (4)
N(1)	3395 (4)	3532 (3)	3274 (3)	3·8 (2)
N(2)	14 (4)	2036 (3)	3495 (3)	4·0 (2)
N(3)	−981 (4)	2583 (3)	1884 (3)	3·9 (2)
N(4)	1480 (4)	1617 (3)	1631 (3)	3·9 (2)
N(5)	2002 (4)	4183 (3)	1514 (3)	4·2 (2)
N(6)	875 (4)	4427 (3)	3202 (3)	4·1 (2)
C(1)	4616 (5)	4597 (4)	3124 (3)	4·5 (2)
C(2)	6163 (5)	4992 (4)	3595 (4)	6·0 (3)
C(3)	6499 (5)	4321 (5)	4291 (4)	6·1 (3)
C(4)	5257 (6)	3273 (5)	4491 (3)	5·4 (3)
C(5)	3729 (5)	2868 (4)	3971 (3)	4·2 (2)
C(6)	2414 (6)	1699 (4)	4184 (4)	5·4 (3)
C(7)	798 (6)	1840 (5)	4405 (3)	5·7 (3)
C(8)	−1560 (5)	1695 (4)	3370 (3)	4·5 (4)
C(9)	−2162 (5)	1967 (4)	2443 (3)	4·3 (2)
C(10)	−2715 (6)	1084 (5)	4128 (4)	6·1 (3)
C(11)	−3913 (5)	1596 (5)	2075 (4)	6·2 (3)
C(12)	536 (5)	455 (4)	1773 (4)	4·8 (3)
C(13)	689 (6)	−554 (4)	1252 (4)	6·1 (3)
C(14)	1816 (7)	−426 (5)	548 (4)	6·7 (3)
C(15)	2748 (6)	752 (5)	364 (4)	6·1 (3)
C(16)	2574 (5)	1773 (4)	913 (3)	4·3 (2)
C(17)	3569 (6)	3050 (5)	693 (3)	5·6 (3)
C(18)	2568 (6)	3840 (4)	546 (3)	5·8 (3)
C(19)	1765 (5)	5197 (4)	1703 (4)	5·0 (2)
C(20)	1168 (5)	5380 (4)	2688 (4)	5·0 (2)
C(21)	2051 (5)	6155 (4)	990 (5)	7·4 (3)
C(22)	953 (7)	6530 (5)	3135 (5)	7·7 (3)

The crystal structure consists of discrete bis{3-[2-(2-pyridyl)ethyl]imino-2-butanone oximato}cobalt(III) cations and perchlorate anions. The atomic labelling of the cation is shown in Fig. 1. The Co atom is coordinated to six N atoms of two tridentate ligand molecules in a slightly distorted octahedral arrangement. Each ligand is coordinated to form a five-membered chelate ring involving the oxime N and imino N atoms and a six-membered chelate ring involving the imino N and pyridine N atoms. The angles around the Co atom deviate from 90° by 0·5 to 8·2°, the five-membered rings having the largest deviations from 90°. The pyridine rings seem to repel each other, as suggested by the opening of the N(1)—Co—N(4) angle and closing of the N(3)—Co—N(6) angle.

The four C—N bonds in the five-membered chelate rings, whose lengths average 1·306 (9) Å, can be regarded as being of two types: N(2)—C(8) and N(5)—C(19) with average length 1·291 (4) Å, and N(3)—C(9) and N(6)—C(20) with average length 1·322 (4) Å. The two C(sp^2)—C(sp^2) single bonds average 1·449 (5) Å. The C—N bonds are longer and the C—C bonds are shorter than the corresponding distances in bis(acetonitrile)-bis-μ-{3-[2-(2-pyridyl)-ethyl]imino-2-butanone oximato-*N,N′,N″,O*}-di-copper(II) (Bertrand *et al.,* 1977) and in (dimethylglyoximato)copper(II) (Vaciago & Zamibonelli, 1970). The present values indicate some degree of cyclic delocalization in the ring.

The pyridine and the 3-imino-2-butanone oxime fragments are almost planar. The maximum deviations are 0·021 (5) Å for C(1) and 0·017 (4) Å for N(4) in the pyridine planes, and 0·052 (5) Å for C(10) and 0·064 (4) Å for N(5) in the oxime planes. The dihedral angles between the pyridine and 3-imino-2-butanone oxime planes are 29·9 (3) and 30·9 (3)°.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38452 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

Co—N(1)	2·032 (4)	Co—N(4)	2·043 (4)
Co—N(2)	1·929 (4)	Co—N(5)	1·927 (4)
Co—N(3)	1·913 (4)	Co—N(6)	1·918 (4)
N(1)—C(1)	1·353 (5)	N(4)—C(12)	1·348 (5)
C(1)—C(2)	1·375 (6)	C(12)—C(13)	1·371 (7)
C(2)—C(3)	1·369 (8)	C(13)—C(14)	1·362 (8)
C(3)—C(4)	1·367 (7)	C(14)—C(15)	1·376 (7)
C(4)—C(5)	1·388 (6)	C(15)—C(16)	1·407 (8)
C(5)—N(1)	1·363 (6)	C(16)—N(4)	1·353 (6)
C(5)—C(6)	1·493 (6)	C(16)—C(17)	1·496 (7)
C(6)—C(7)	1·526 (8)	C(17)—C(18)	1·522 (9)
C(7)—N(2)	1·459 (6)	C(18)—N(5)	1·470 (6)
N(2)—C(8)	1·292 (5)	N(5)—C(19)	1·290 (6)
C(8)—C(9)	1·442 (6)	C(19)—C(20)	1·454 (7)
C(8)—C(10)	1·493 (7)	C(19)—C(21)	1·501 (8)
C(9)—C(11)	1·491 (6)	C(20)—C(22)	1·506 (8)
C(9)—N(3)	1·323 (5)	C(20)—N(6)	1·320 (6)
N(3)—O(1)	1·268 (5)	N(6)—O(2)	1·265 (5)
Cl—O(3)	1·427 (6)	Cl—O(5)	1·414 (6)
Cl—O(4)	1·414 (6)	Cl—O(6)	1·438 (5)
N(1)—Co—N(2)	93·3 (2)	N(4)—Co—N(5)	94·1 (2)
N(1)—Co—N(3)	174·5 (2)	N(4)—Co—N(6)	175·2 (2)
N(1)—Co—N(5)	94·7 (1)	N(4)—Co—N(2)	94·3 (2)
N(1)—Co—N(6)	89·8 (2)	N(4)—Co—N(3)	90·5 (2)
N(1)—Co—N(4)	93·1 (1)	N(3)—Co—N(6)	86·9 (2)
N(2)—Co—N(3)	82·2 (2)	N(5)—Co—N(6)	81·8 (2)
N(2)—Co—N(6)	89·3 (2)	N(3)—Co—N(5)	89·2 (2)
N(2)—Co—N(5)	168·0 (2)		
Co—N(1)—C(1)	119·1 (3)	Co—N(4)—C(12)	118·9 (3)
Co—N(1)—C(5)	124·1 (2)	Co—N(4)—C(16)	123·5 (3)
Co—N(2)—C(7)	124·0 (3)	Co—N(5)—C(18)	122·5 (3)
Co—N(2)—C(8)	113·6 (3)	Co—N(5)—C(19)	114·2 (3)
Co—N(3)—C(9)	114·4 (3)	Co—N(6)—C(20)	115·0 (3)
Co—N(3)—O(1)	124·0 (3)	Co—N(6)—O(2)	122·9 (3)
N(1)—C(1)—C(2)	123·4 (5)	N(4)—C(12)—C(13)	122·8 (4)
C(1)—C(2)—C(3)	119·7 (4)	C(12)—C(13)—C(14)	121·0 (4)
C(2)—C(3)—C(4)	117·8 (4)	C(13)—C(14)—C(15)	117·1 (5)
C(3)—C(4)—C(5)	121·2 (5)	C(14)—C(15)—C(16)	120·8 (5)
C(4)—C(5)—N(1)	121·0 (4)	C(15)—C(16)—N(4)	120·7 (4)
C(1)—N(1)—C(5)	116·8 (4)	C(12)—N(4)—C(16)	117·6 (4)
N(1)—C(5)—C(6)	119·1 (4)	N(4)—C(16)—C(17)	118·9 (4)
C(4)—C(5)—C(6)	119·9 (5)	C(15)—C(16)—C(17)	120·4 (4)
C(5)—C(6)—C(7)	113·3 (4)	C(16)—C(17)—C(18)	114·1 (4)
C(6)—C(7)—N(2)	111·0 (4)	C(17)—C(18)—N(5)	110·6 (4)
C(7)—N(2)—C(8)	121·6 (4)	C(18)—N(5)—C(19)	122·4 (4)
N(2)—C(8)—C(9)	115·6 (4)	N(5)—C(19)—C(20)	115·3 (5)
N(2)—C(8)—C(10)	123·7 (4)	N(5)—C(19)—C(21)	124·9 (5)
C(9)—C(8)—C(10)	120·7 (4)	C(20)—C(19)—C(21)	119·8 (5)
C(8)—C(9)—C(11)	126·7 (4)	C(19)—C(20)—C(22)	125·9 (5)
C(8)—C(9)—N(3)	113·4 (4)	C(19)—C(20)—N(6)	112·8 (4)
C(11)—C(9)—N(3)	119·9 (4)	C(22)—C(20)—N(6)	121·3 (5)
C(9)—N(3)—O(1)	121·6 (4)	C(20)—N(6)—O(2)	122·1 (4)
O(3)—Cl—O(4)	108·6 (3)	O(4)—Cl—O(5)	111·5 (4)
O(3)—Cl—O(5)	108·0 (3)	O(4)—Cl—O(6)	110·0 (3)
O(3)—Cl—O(6)	109·5 (4)	O(5)—Cl—O(6)	109·3 (3)

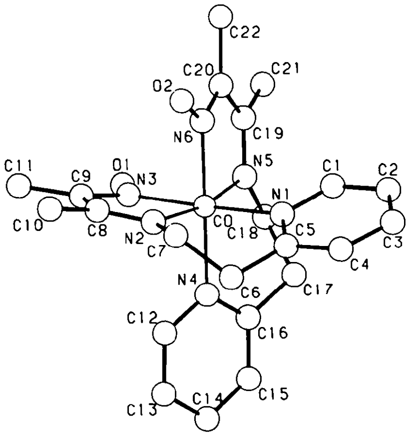

Fig. 1. Perspective view of the complex cation.

The perchlorate ion has an average Cl—O distance of 1·423 (3) Å and average O—Cl—O angle of 109·5 (1)°, both of which are normal for this ion.

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Thiaminium Tetrachlorocobaltate(II) Monohydrate,* $C_{12}H_{18}N_4OS^{2+}.CoCl^2{}_4{}^-.H_2O$

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Abstract. $M_r = 485 \cdot 12$, monoclinic, $P2_1/n$, $a = 16 \cdot 518$ (1), $b = 15 \cdot 445$ (1), $c = 7 \cdot 883$ (1) Å, $\beta = 97 \cdot 55$ (1)°, $V = 1993 \cdot 8$ Å^3, $Z = 4$, $D_m = 1 \cdot 61$, $D_x = 1 \cdot 62$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda(\alpha_1) = 0 \cdot 70926$ Å, $\mu = 15 \cdot 4$ cm^{-1}, $F(000) = 988$, room temperature, $R = 0 \cdot 035$ for 3032 reflections with $I > 3\sigma(I)$, $R = 0 \cdot 049$ for all 3507 reflections. The compound is isostructural with thiaminium tetrachlorocadmate monohydrate, with the thiaminium cation in the S conformation. The $CoCl_4^{2-}$ ion is tetrahedral with an average Co—Cl bond length of 2·276 (16) Å.

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* The thiamine cation is 3-[(4-amino-2-methyl-5-pyrimidinyl)methyl]-5-(2-hydroxyethyl)-4-methylthiazolium.

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