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Structures of Two Pyridine Alkylcobaloximes with Alkyl = Cyanomethyl and Benzyl

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Abstract. (I) *trans*-(Cyanomethyl)(dimethylglyoximato)(dimethylglyoxime)(pyridine)cobalt(III), $[Co(C_4H_6N_2O_2)(C_4H_8N_2O_2)(CH_2CN)(C_5NH_5)]$, $M_r = 408·3$, triclinic, $P\bar{1}$, $a = 9·057\ (1)$, $b = 14·673\ (2)$, $c = 7·517\ (1)$ Å, $\alpha = 96·76\ (1)$, $\beta = 99·78\ (1)$, $\gamma = 107·64\ (1)$°, $V = 922·8\ (2)$ Å^3, $Z = 2$, $D_x = 1·47$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0·90$ mm^{-1}, $F(000) = 424$, $T = 293$ K, $R = 0·038$ for 1579 unique observed reflections. (II) *trans*-Benzylbis(dimethylglyoximato)(pyridine)cobalt(III), $[Co(C_4H_7N_2O_2)_2(C_7H_7)(C_5NH_5)]$, $M_r = 459·4$, triclinic, $P\bar{1}$, $a = 8·298\ (1)$, $b = 10·250\ (1)$, $c = 13·527\ (1)$ Å, $\alpha = 99·86\ (1)$, $\beta = 98·44\ (1)$, $\gamma = 108·50\ (1)$°, $V = 1049·7\ (2)$ Å^3, $Z = 2$, $D_x = 1·45$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0·80$ mm^{-1}, $F(000) = 480$, $T = 293$ K, $R = 0·034$ for 2477 unique observed reflections. The axial fragment of the distorted octahedral polyhedron of Co is characterized by Co—C and Co—N distances of 2·024 (6) and 2·014 (4) Å in (I) and 2·065 (4) and 2·056 (3) Å in (II). The different electronic and steric properties of the two alkyl groups are discussed.

Introduction. Simple model molecules of the B_{12} system such as cobaloximes, the trivial name of the organometallic complexes $LCo(DH)_2R$, where R = alkyl group, DH = monoanion of dimethylglyoxime and L = neutral Lewis base, have proved very useful in suggesting a possible mechanism for Co—C bond cleavage (Halpern, 1985; Bresciani Pahor, Forcolin, Marzilli, Randaccio, Summers & Toscano, 1985). Extensive structural studies on cobaloximes have been carried out in recent years and relationships with solution properties have been established (Bresciani Pahor, Forcolin, Marzilli, Randaccio, Summers & Toscano, 1985). Thus, it has been shown that Co—L distances reflect essentially the σ-donor power of the R group (*trans* influence), increasing by 0·2 Å from R = CN to R = adamantyl for the same L. Analogously, the Co—C bond length mainly reflects the bulk of R, increasing by 0·2 Å from R = Me to R = adamantyl. On the other hand, although qualitative relationships appear to be clarified (Zangrando, Bresciani Pahor, Randaccio, Charland & Marzilli, 1986; Marzilli, Bayo, Summers, Thomas, Zangrando, Bresciani Pahor, Mari & Randaccio, 1987), quantitative aspects are needed to be investigated requiring more structural data. As part of this extensive study, we report the crystal structures of two complexes with L = py and R = CH_2CN (I) and CH_2Ph (II).

Experimental. Crystals 0·20 × 0·15 × 0·06 mm (I) and 0·42 × 0·23 × 0·12 mm (II). Enraf–Nonius CAD-4 single-crystal diffractometer, graphite-monochromated Mo $K\alpha$. Lattice constants by least-squares refinement of 25 setting angles with $12 \leq \theta \leq 20°$, three standard reflections measured every 4000 s showed no significant intensity decay, $\omega/2\theta$ scan, scan angle $(0·70 + 0·35\tan\theta)°$ (I) and $(1·1 + 0·35\tan\theta)°$ (II), 4776 reflections measured in the range $4 \leq 2\theta \leq 56°$, $-11 \leq h \leq 11$, $-17 \leq k \leq 14$, $0 \leq l \leq 9$ for (I) and 5288 in the range $4 \leq 2\theta \leq 56°$, $-10 \leq h \leq 10$, $-13 \leq k \leq 12$, $0 \leq l \leq 17$ for (II), 1579 (I) and 2477 (II) independent reflections with $I \geq 2\sigma(I)$ for (I) and $I \geq 3\sigma(I)$ for (II) used for structure determination, intensities corrected for Lorentz and polarization factors, empirical absorption correction based on the ψ scan, min./max. transmission 0·95/0·99. Structure solved by Patterson method, Fourier syntheses and full-matrix least squares on F, 237 (I) and 273 (II) parameters refined, anisotropic temperature factors for all non-H atoms, H atoms located on difference Fourier map, refined through some least-squares cycles with reflections having $(\sin\theta)/\lambda < 0·40$ Å^{-1} and included as fixed contributors in the final least-squares cycle, $R = 0·038$, $wR = 0·042$, $w = 1·00/[\sigma^2(F) + 6·4 \times 10^{-4}F^2]$ for (I) and $R = 0·034$, $wR = 0·038$, $w = 1·08/[\sigma^2(F) + 5·0 \times 10^{-4}F^2]$ for (II), the final difference maps had max. ±0·25 e Å^{-3}. Neutral scattering factors, including anomalous-dispersion terms for all non-H atoms, from *International Tables for X-ray Crystallography* (1974), no correction for secondary extinction, all calculations

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Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters for* $pyCo(D)(DH_2)CH_2CN$

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

	x	y	z	B_{eq}(Å^2)
Co	0·4175 (1)	0·21426 (6)	0·3129 (1)	2·45 (3)
O(1)	0·6391 (5)	0·3171 (3)	0·1190 (5)	3·8 (2)
O(2)	0·3664 (5)	0·2750 (3)	0·6603 (5)	4·2 (2)
O(3)	0·2019 (6)	0·1053 (3)	0·5067 (6)	5·1 (2)
O(4)	0·4772 (5)	0·1486 (3)	−0·0338 (6)	4·3 (2)
N(1)	0·5807 (5)	0·3193 (4)	0·2725 (6)	2·8 (2)
N(2)	0·4482 (6)	0·2998 (4)	0·5320 (6)	3·0 (2)
N(3)	0·2582 (6)	0·1064 (4)	0·3516 (7)	3·5 (2)
N(4)	0·3919 (6)	0·1267 (4)	0·0950 (6)	3·1 (2)
N(5)	0·2512 (5)	0·2646 (3)	0·1876 (5)	2·4 (2)
N(6)	0·8569 (8)	0·2759 (5)	0·5563 (8)	6·9 (4)
C(1)	0·7675 (8)	0·4840 (5)	0·394 (1)	5·5 (4)
C(2)	0·6377 (7)	0·3951 (5)	0·4024 (8)	2·9 (3)
C(3)	0·5619 (7)	0·3827 (4)	0·5572 (8)	3·1 (3)
C(4)	0·6123 (8)	0·4550 (5)	0·7325 (9)	5·0 (3)
C(5)	0·0845 (9)	−0·0633 (5)	0·238 (1)	5·9 (4)
C(6)	0·2062 (8)	0·0285 (5)	0·225 (1)	3·7 (3)
C(7)	0·2851 (8)	0·0417 (5)	0·0703 (9)	3·5 (3)
C(8)	0·2481 (8)	−0·0343 (5)	−0·0962 (9)	5·5 (3)
C(9)	0·5714 (8)	0·1580 (5)	0·4503 (8)	4·2 (3)
C(10)	0·7295 (9)	0·2219 (5)	0·5090 (8)	4·2 (3)
C(11)	0·1299 (7)	0·2725 (4)	0·2656 (8)	3·3 (3)
C(12)	0·0136 (7)	0·3037 (5)	0·1800 (9)	3·8 (3)
C(13)	0·0154 (7)	0·3275 (4)	0·0089 (9)	4·0 (3)
C(14)	0·1391 (7)	0·3189 (4)	−0·0714 (7)	3·5 (3)
C(15)	0·2532 (6)	0·2892 (4)	0·0206 (7)	2·9 (2)

Table 2. *Final fractional coordinates and equivalent isotropic thermal parameters for* $pyCo(DH)_2CH_2C_6H_5$

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

	x	y	z	B_{eq}(Å^2)
Co	0·21584 (6)	0·31328 (5)	0·23318 (4)	2·50 (2)
O(1)	0·0469 (4)	0·2912 (3)	0·0299 (2)	4·4 (1)
O(2)	0·1433 (4)	0·4291 (3)	0·4212 (2)	4·7 (1)
O(3)	0·3768 (3)	0·3276 (3)	0·4365 (2)	4·0 (1)
O(4)	0·2763 (4)	0·1838 (3)	0·0453 (2)	4·4 (1)
N(1)	0·0564 (4)	0·3370 (3)	0·1305 (2)	3·3 (1)
N(2)	0·1036 (4)	0·4031 (3)	0·3181 (2)	3·3 (1)
N(3)	0·3689 (4)	0·2839 (3)	0·3363 (2)	2·7 (1)
N(4)	0·3219 (4)	0·2156 (3)	0·1489 (2)	3·1 (1)
N(5)	0·3972 (3)	0·5057 (3)	0·2362 (2)	2·7 (1)
C(1)	−0·1792 (6)	0·4289 (5)	0·0893 (4)	6·2 (3)
C(2)	−0·0469 (5)	0·4004 (4)	0·1607 (3)	3·8 (2)
C(3)	−0·0200 (5)	0·4386 (4)	0·2725 (3)	3·7 (2)
C(4)	−0·1268 (6)	0·5074 (5)	0·3264 (5)	6·0 (3)
C(5)	0·5888 (6)	0·1780 (5)	0·3778 (4)	5·6 (2)
C(6)	0·4670 (4)	0·2157 (4)	0·3065 (3)	3·4 (2)
C(7)	0·4376 (5)	0·1742 (4)	0·1950 (3)	3·4 (2)
C(8)	0·5284 (6)	0·0894 (5)	0·1400 (4)	5·9 (2)
C(9)	0·0254 (5)	0·1217 (4)	0·2243 (3)	3·5 (2)
C(10)	0·0830 (4)	0·0156 (4)	0·2651 (3)	3·0 (1)
C(11)	0·0989 (5)	0·0130 (4)	0·3686 (3)	3·9 (2)
C(12)	0·1552 (6)	−0·0837 (5)	0·4075 (4)	5·3 (2)
C(13)	0·1981 (6)	−0·1808 (5)	0·3456 (5)	5·8 (3)
C(14)	0·1817 (6)	−0·1840 (5)	0·2443 (4)	5·4 (2)
C(15)	0·1227 (5)	−0·0874 (4)	0·2022 (3)	4·2 (2)
C(16)	0·4304 (5)	0·5436 (4)	0·1482 (3)	3·2 (2)
C(17)	0·5502 (5)	0·6713 (5)	0·1479 (3)	4·3 (2)
C(18)	0·6415 (5)	0·7643 (4)	0·2389 (4)	4·3 (2)
C(19)	0·6080 (5)	0·7276 (4)	0·3292 (3)	4·3 (2)
C(20)	0·4859 (5)	0·5987 (4)	0·3244 (3)	3·3 (1)

on a Cray X-MP/12 computer by using the *SHELX*76 (Sheldrick, 1976) system of programs.

Table 3. *Selected bond distances* (Å) *and bond angles* (°)

	$pyCo(D)(DH_2)CH_2CN$	$pyCo(DH)_2CH_2C_6H_5$
Co—N(1)	1·880 (5)	1·876 (3)
Co—N(2)	1·874 (5)	1·879 (3)
Co—N(3)	1·882 (5)	1·875 (3)
Co—N(4)	1·893 (5)	1·881 (3)
Co—N(5)	2·014 (4)	2·056 (3)
Co—C(9)	2·024 (6)	2·065 (4)
O(1)—N(1)	1·350 (5)	1·343 (4)
N(1)—C(2)	1·297 (7)	1·299 (5)
C(2)—C(1)	1·484 (8)	1·488 (5)
C(2)—C(3)	1·450 (8)	1·461 (6)
C(3)—C(4)	1·497 (8)	1·491 (6)
C(3)—N(2)	1·302 (7)	1·301 (5)
N(2)—O(2)	1·332 (5)	1·345 (4)
O(3)—N(3)	1·349 (6)	1·339 (4)
N(3)—C(6)	1·305 (7)	1·294 (5)
C(6)—C(5)	1·487 (9)	1·481 (5)
C(6)—C(7)	1·464 (8)	1·456 (6)
C(7)—C(8)	1·492 (8)	1·495 (5)
C(7)—N(4)	1·294 (8)	1·290 (4)
N(4)—O(4)	1·347 (6)	1·350 (4)
C(9)—C(10)	1·414 (9)	1·474 (5)
N(1)—Co—N(2)	81·8 (2)	81·5 (1)
N(1)—Co—N(3)	178·1 (2)	177·9 (1)
N(1)—Co—N(4)	98·0 (2)	98·9 (1)
N(1)—Co—N(5)	91·1 (2)	91·1 (1)
N(1)—Co—C(9)	93·2 (2)	86·0 (1)
N(2)—Co—N(3)	99·3 (2)	98·2 (1)
N(2)—Co—N(4)	178·2 (2)	177·5 (1)
N(2)—Co—N(5)	91·1 (2)	90·6 (1)
N(2)—Co—C(9)	87·6 (2)	89·1 (1)
N(3)—Co—N(4)	80·8 (2)	81·4 (1)
N(3)—Co—N(5)	90·4 (2)	90·9 (1)
N(3)—Co—C(9)	85·4 (2)	92·0 (1)
N(4)—Co—N(5)	90·7 (2)	91·9 (1)
N(4)—Co—C(9)	90·7 (2)	88·4 (1)
N(5)—Co—C(9)	175·2 (2)	177·1 (1)
Co—C(9)—C(10)	115·1 (5)	116·7 (2)

Discussion. Final atomic coordinates and thermal parameters of both compounds are given in Tables 1 and 2.* Selected bond lengths and angles are listed in Table 3. *ORTEP* (Johnson, 1965) drawings of molecules (I) and (II) with the labeling scheme are depicted in Figs. 1 and 2, respectively. Both complexes crystallize with discrete molecules, in which the cobalt atom exhibits a distorted octahedral stereochemistry, with four oxime N-donors in the equatorial positions.

Compound (I) has the two equatorial dimethylglyoxime ligands present as dianionic (D^{2-}) and neutral (DH_2) species. Previous structural investigations of bis(dimethylglyoximato)Co^{III} complexes have shown that this ligand more often acts as monoanionic (DH^-) species (Bresciani Pahor, Forcolin, Marzilli, Randaccio, Summers & Toscano, 1985). As previously observed for the $ClCo(D)(DH_2)$(sulfanilamide) and $ClCo(D)(DH_2)$(4-chloroaniline) complexes (Palenik, Sullivan &

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* Lists of structure factors, anisotropic thermal parameters for non-hydrogen atoms, atomic parameters for hydrogen atoms, bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51207 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Najk, 1976) there is a small but significant lengthening of the Co—N bond distances of the DH_2 unit [mean value 1·888 (5) Å] with respect to those of the D^{2-} [mean value 1·877 (5) Å]. The four oxime N donors are coplanar within ±0·002 Å and the cobalt atom is displaced 0·027 Å from their mean plane towards pyridine. The dimensions of the D^{2-} and DH_2 moieties, planar within ±0·06 Å, are quite normal and the dihedral angle, α, between their mean planes is +4·7° (the positive sign of α denotes a bending towards the alkyl group). The py—Co—CH_2CN axial fragment is characterized by Co—C and Co—N bond distances of 2·024 (6) and 2·014 (4) Å, respectively, with a C—Co—N angle of 175·2 (2)°. The value of the axial Co—N distance confirms the previous findings that the Co—N(py) bond length in $pyCo(DH)_2CH_2X$ complexes is strongly affected by the electronic nature of the X substituent. The σ-donor power of the Co-bonded carbon atom is significantly decreased by a strong electron-withdrawing substituent such as CN, and approaches that of the non-alkyl groups. A Co—N bond distance of 1·973 (5) Å was reported for $pyCo(DH)_2N_3$ (Clearfield, Gopal, Kline, Sipaki & Urban, 1978), which should be compared with that of 2·099 (2) Å in $pyCo(DH)_2{}^iPr$ (Marzilli, Toscano, Randaccio, Bresciani Pahor & Calligaris, 1979). Since the Co—C bond distance lengthens with the increasing bulk of the alkyl group from 1·998 (5) Å (R = Me) to 2·160 (4) Å (R = adamantyl) (Bresciani Pahor, Forcolin, Marzilli, Randaccio, Summers & Toscano, 1985), the present value of 2·024 (6) Å falls within the range expected for a slightly bulky CH_2X derivative (Randaccio, Bresciani Pahor, Toscano & Marzilli, 1981).

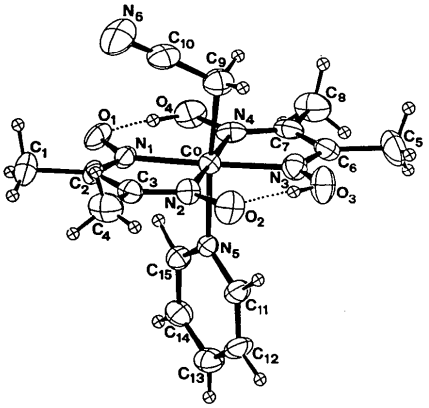

Fig. 1. *ORTEP* drawing and labeling scheme for non-H atoms of $pyCo(D)(DH_2)CH_2CN$ (thermal ellipsoids 40%). Hydrogen atoms are represented as spheres of radius 0·10 Å.

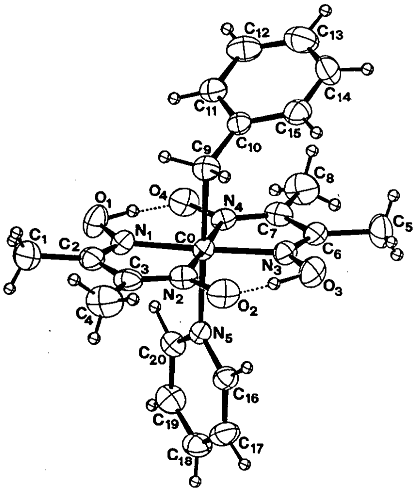

Fig. 2. *ORTEP* drawing and labeling scheme for non-H atoms of $pyCo(DH)_2CH_2Ph$ (thermal ellipsoids 40%). Hydrogen atoms are represented as spheres of radius 0·10 Å.

The dimensions of the equatorial moiety of (II), which contains two DH^- monoanions, are only slightly different from those of (I) (see above). The four oxime N-donors are coplanar within ±0·04 Å and the displacement of the Co atom out of their mean plane towards the axial N is 0·037 Å. The two DH^- halves are planar within ±0·03 Å and the bending angle α is +4·9°. The Co—C and Co—N(axial) bond lengths are 2·065 (4) and 2·056 (3) Å, respectively, and the C—Co—N(axial) angle 177·1 (1)°. As expected, the Co—py distance in (II) is significantly longer than that found in (I), but is very close to the value of 2·068 (3) Å reported for the Me analogue (Bresciani Pahor, Forcolin, Marzilli, Randaccio, Summers & Toscano, 1985). Similar results have been found for the Costa model system, $\{H_2OCo[(DO)(DOH)pn]R\}^+$, with (DO)(DOH)pn = 3,3′-(1,3-propanediyldinitrilo)di(2-butanone oximato), where the values of the Co—OH_2 bond length are 2·103 (3) and 2·099 (1) Å when R is Me and CH_2Ph, respectively. However, on the basis of the expected electronic σ-donor power of the two R groups, a slightly longer Co—py distance should be predicted in the benzyl derivatives. The Co—C bond distance of 2·065 (4) Å in (II) compared with that of 2·060 (6) Å observed in $pyCo(DH)_2CH_2CMe_3$ (Bresciani Pahor, Forcolin, Marzilli, Randaccio, Summers & Toscano, 1985) suggests that the extent of the steric interaction of the benzyl group with the equatorial ligands is close to that of neopentyl, although the effective bulk of the alkyl is significantly reduced by the distortion of the Co—CH_2—C angle, which is 130·3 (6)° in the CH_2CMe_3 derivative and 116·7 (2)° in (II). The bonding geometry of the Co—CH_2X fragment in these two compounds may be ascribed to different interactions of the *tert*-butyl and phenyl residues with the equatorial moiety. If we assume that localized π–π interactions between the DH ligand and the CH_2Ph phenyl group occur (Fig. 2), the Co—CH_2—Ph angle cannot be opened to a large extent as happens in the neopentyl analogue. As a consequence, the Co—C distance in (II) should lengthen to a value very close to that of the CH_2CMe_3 derivative in order to minimize the steric repulsion with the equatorial N-donors. A similar value for the Co—C distance [2·052 (2) Å] was found in {$H_2OCo[(DO)(DOH)pn]$-CH_2Ph}$^+$ (Zangrando, Parker, Bresciani Pahor, Thomas, Marzilli & Randaccio, 1987).

In both structures (I) and (II) the py ligand, planar within ±0·009 and ±0·006 Å, respectively, has the orientation usually found in pyCo$(DH)_2R$ compounds, *i.e.* nearly perpendicular to the equatorial coordination plane and bisecting the oxime bridges. A very short O···C(py) van der Waals distance of 3·06 Å was observed in (I).

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Structure of 2-Carboxyanilinium Dihydrogenmonoarsenate

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Abstract. $C_7H_8NO_2^+.H_2AsO_4^-$, $M_r = 279·08$, monoclinic, $P2_1/c$, $a = 9·867$ (2), $b = 10·827$ (3), $c = 9·305$ (2) Å, $\beta = 100·19$ (5)°, $V = 978·4$ (8) Å^3, $Z = 4$, $D_x = 1·894$ Mg m^{-3}, λ(Ag $K\alpha$) = 0·5608 Å, $\mu = 1·951$ mm^{-1}, $F(000) = 560$, $T = 295$ K, final $R = 0·025$ for 3230 unique reflexions. Planes of $H_2AsO_4^-$ tetrahedra alternate with sheets of $C_7H_8NO_2^+$ cations in a centrosymmetrical framework. The two-dimensional network of $H_2AsO_4^-$ is held together through hydrogen bonds.

Introduction. The reactions between ethanolic solutions of anthranilic acid, 3-aminobenzoic acid or 4-aminobenzoic acid and monophosphoric or monoarsenic acid water solutions yield compounds corresponding to the formulas $C_7H_5O_2(NH_2).H_3XO_4$ or $C_7H_5O_2(NH_2).H_3XO_4.H_2O$ (X = P, As). Crystals obtained with phosphoric acid are air sensitive, while the corresponding arsenic salts are stable under normal conditions. The monoarsenates of the three aminobenzoic acid isomers have been crystallized. The present paper and the following one (Tordjman, Masse & Guitel, 1988) describe the structures of the two forms $C_7H_8NO_2^+.H_2AsO_4^-$ and $C_7H_8NO_2^+.H_2AsO_4^-.H_2O$.

Experimental. An ethanolic solution of anthranilic acid was mixed with an aqueous solution of H_3AsO_4 in a stoichiometric ratio. The final solution was concentrated at 343 K and slowly evaporated at room temperature.

Crystals appeared as large tabular monoclinic prisms up to 5 mm long. Crystal size used for data collection: 0·48 × 0·48 × 0·30 mm. Density not measured. Enraf–Nonius CAD-4 diffractometer, graphite monochromator. Extinction rules: $h0l$, $l = 2n$, $0k0$, $k = 2n$. 21 reflexions ($11 < \theta < 14°$) used for refining unit-cell dimensions. ω scan. 4962 non-zero unique reflexions collected ($3 < \theta < 27·5°$). $\pm h,k,l$, $h_{max} = 16$, $k_{max} = 17$, $l_{max} = 15$. Scan width 1·20°, scan speed from 0·02 to 0·06° s^{-1}, total background measuring time: 10 to 27 s.

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