The arrangement of donor atoms around the central atom is influenced by the steric properties of the 2,4-dimethylpyridine ligand: the 2-methyl substituents, *i.e.* the pairs of diad-related C(26) and C(15) methyl groups, block further coordination of the Ni atom; the intramolecular distances Ni···C(26) and Ni···C(15) are 3·20 (1) and 3·48 (3) Å, respectively. Two C(26) methyl groups lie approximately in the position *trans* to N(1), while the two disordered C(15) methyl groups occupy the space between the N(1) atom and the N atoms of the NCS groups.

The N(1) pyridine atoms N(1), C(13) and C(14) lie on a crystallographic twofold axis, with consequent disordering of both methyl substituents. The high $U_{\rm eq}$ values for some of the C atoms of this ring (Table 1) may also reflect the disorder.

The N(2) pyridine ring is planar, the N(1) pyridine atoms deviate significantly from planarity [C(11) and C(12) atoms by 0·02 (1) and 0·03 (2) Å, respectively]; their average planes form a dihedral angle of 71·1 (6)°.

The shortest contacts were found between the S and H atoms [H atoms bonded to the C(24) and C(12) atoms] of the adjacent complex molecules; further contacts were found between 2,4-dimethylpyridine ligands of adjacent molecules. Intermolecular contacts correspond to the sum of the van der Waals radii of the atoms involved.

References

Addison, A. W., Nageswara Rao, T., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* p. 1349.

Andreetti, G. D., Bocelli, G. & Sgarabotto, P. (1972). *Cryst. Struct. Commun.* **1**, 51–54.

Ďurčanská, E., Głowiak, T. & Kožíšek, J. (1982). *Chem. Zvesti*, **36**, 651–660.

Ďurčanská, E., Jamnický, M., Koman, M., Wnęk, I. & Głowiak, T. (1986). *Acta Cryst.* C**42**, 1157–1159.

Jóna, E., Jamnický, M. & Šramko, T. (1978). *Z. Anorg. Allg. Chem.* **447**, 207–214.

Kerr, I. S. & Williams, D. (1977). *Acta Cryst.* B**33**, 3589–3592.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Syntex (1973). *XTL Structure Determination System*. Syntex Analytical Instruments, Cupertino, California, USA.

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Synthesis and Structure of Bis(tetraphenylphosphonium) Bis(tetratellurido)palladate Dimethylformamide Solvate

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Abstract. $[P(C_6H_5)_4]_2[Pd(Te_4)_2].C_3H_7NO$ (I), M_r = 1806, orthorhombic, *Pbca*, a = 29·611 (10), b = 16·291 (6), c = 23·325 (9) Å, V = 11251·8 Å^3, Z = 8, D_x = 2·17, D_m = 2·20 (1) g cm^{-3} (by flotation in $CHBr_3$/heptane), Mo $K\alpha$, λ = 0·71069 Å, μ = 44·9 cm^{-1}, $F(000)$ = 6680, T = 296 K, final R = 0·044, wR = 0·049 for 4453 reflections with $F_o^2 > 3\sigma(F_o^2)$. The structure is composed of Ph_4P^+ cations, $[Pd(Te_4)_2]^{2-}$ anions and DMF molecules. The $[Pd(Te_4)_2]^{2-}$ complex features a nearly square-planar Pd^{2+} atom chelated by two Te_4^{2-} ligands. The $PdTe_4$ five-membered rings are puckered forming an envelope conformation. The mean Pd—Te bond distance is 2·587 (2) Å. The mean Te—Te bond distance is 2·74 (3) Å.

Introduction. Transition-metal polytelluride chemistry is relatively little explored. Recently reports of some remarkable species $[Hg_4Te_{12}]^{4-}$ and $[Hg_2Te_5]^{2-}$ (Haushalter, 1985*a*), $[NbTe_{10}]^{3-}$ (Flomer & Kolis, 1988), $[Mo_4Te_{16}(en)_4]^{2-}$ (Eichhorn, Haushalter, Cotton & Wilson, 1988), $[Fe_2(CO)_6Te_3]^{2-}$ (Eichhorn & Haushalter, 1990), $[Cr(CO)_2(Te_2)_2]^{2-}$ (Flomer, O'Neal, Kolis, Jeter & Cordes, 1988), $[Au_2Te_2]^{2-}$ (Haushalter, 1985*b*), and $[KAu_9Te_7]^{4-}$ and $[K_2Au_4Te_4(solv)_4]^{2-}$ (Haushalter, 1985*c*) indicate that polytelluride chemistry will produce new compounds, not quite analogous to S or even Se. As part of our synthetic efforts in this area we synthesized and structurally characterized $[Pd(Te_4)_2]^{2-}$ as the Ph_4P^+ salt. While our work was in progress (Kanatzidis, 1988), the structure of $(Ph_4P)_2[Pd(Te_4)_2]$ was reported (Adams, Wolfe, Eichhorn & Haushalter, 1989). Interestingly, although the molecular structure of Haushalter's $[Pd(Te_4)_2]^{2-}$ is essentially the same as ours, the space groups in the two varieties are different. Our complex (I) is a dimethylformamide (DMF) solvate and has an orthorhombic crystal system, whereas Haushalter's compound (II) is unsolvated and is triclinic. Since (I) is different, we wish to

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report the crystal structure of this new solvated modification.

Experimental. All work was performed in a glovebox (Vacuum Atmospheres, Inc.) under a nitrogen atmosphere. Dimethylformamide (DMF) was stored over 4A Linde molecular sieves for several days and distilled under vacuum. Ether was distilled over sodium (or potassium)/benzophenone under a nitrogen blanket. Li_2PdCl_4 was purchased from Alpha Products. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Satisfactory elemental analyses were obtained. Sodium tetratelluride (Na_2Te_4) was prepared in liquid ammonia from Na metal and elemental Te in a 2:4 ratio.

A 10 cm^3 DMF solution of 0·051 g (~0·19 mmol) Li_2PdCl_4 was added to a 50 cm^3 DMF solution of 0·220 g (~0·40 mmol) Na_2Te_4 in the presence of 0·150 g (0·40 mmol) Ph_4PCl. Color change from purple to dark brown occurred immediately. After stirring for *ca* 30 min the solution was filtered to remove the NaCl precipitate. Slow addition of *ca* 60 cm^3 ether and storage at room temperature for four days afforded analytically pure black parallelpipeds of $(Ph_4P)_2[Pd(Te_4)_2].C_3H_7NO$ in 85% yield.

The crystallographic data were collected at ambient temperature on a Nicolet *P*3/*F* four-circle diffractometer using an $\omega/2\theta$-scan mode and monochromated Mo $K\alpha$ radiation. The crystal (0·10 × 0·09 × 0·41 mm) was mounted inside a glass capillary and sealed with the long axis approximately parallel to the φ axis of the diffractometer. The intensities of three check reflections were monitored every 100 reflections and did not show any appreciable decay during the data-collection period. 2θ range 4·0–44·0°, $0 \leq h \leq 31$, $0 \leq k \leq 17$, $0 \leq l \leq 24$, number of data collected 7560, number of unique data 7559, 4453 data used $[F_o^2 > 3\sigma(F_o^2)]$. Min., max. absorption correction 0·76, 0·99, number of variables 312, number of atoms per asymmetric unit (including H) 111, final *R*/*wR* 0·044/0·049. An empirical absorption correction was applied to all data based on ψ scans for seven reflections with $\chi \simeq 90°$. No extinction correction was applied. The structure was solved with direct methods using *SHELXS*86 (Sheldrick, 1985) and was refined with the *SDP* (Frenz, 1978) package of crystallographic programs, using a VAX station 2000 computer. All non-C and non-H atoms were refined anisotropically, C atoms isotropically. H-atom positions were calculated and included in the structure-factor calculation but not refined. The H-atom positions of the DMF molecule were not calculated. The atomic scattering factors were as embedded in *SHELXS*86. There were no significant residual peaks (0·2 e Å^{-3} maximum) in the final difference electron density map. The ratio of the least-squares shift to e.s.d. in the final refinement was less than 0·02. The parameters of all non-H atoms and their estimated standard deviations are shown in Table 1.*

Table 1. *Fractional atomic coordinates and* B_{eq} *values for the non-*H *atoms in* (I) *with e.s.d.'s in parentheses*

	x	*y*	*z*	*B*(Å^2)
Te(1)	0·64517 (5)	0·12911 (8)	0·25573 (6)	3·61 (3)
Te(2)	0·65450 (5)	0·20912 (9)	0·35907 (6)	4·29 (3)
Te(3)	0·56938 (5)	0·26941 (9)	0·35910 (6)	4·27 (3)
Te(4)	0·57645 (4)	0·34554 (8)	0·25359 (6)	3·67 (3)
Te(5)	0·56051 (5)	0·31866 (9)	0·11670 (6)	4·30 (3)
Te(6)	0·60711 (5)	0·32332 (9)	0·01387 (6)	4·38 (3)
Te(7)	0·62354 (6)	0·16062 (9)	0·01150 (6)	4·97 (4)
Te(8)	0·66436 (5)	0·15642 (9)	0·11796 (6)	4·08 (3)
Pd	0·61192 (5)	0·23723 (9)	0·18618 (6)	3·02 (3)
P(1)	0·4041 (2)	0·3154 (3)	0·4637 (2)	3·5 (1)
P(2)	0·1678 (2)	0·6227 (3)	0·2548 (2)	3·3 (1)
C(1)	0·4196 (6)	0·361 (1)	0·3966 (8)	3·5 (4)*
C(2)	0·4122 (8)	0·442 (1)	0·387 (1)	5·2 (5)*
C(3)	0·4252 (8)	0·479 (1)	0·337 (1)	5·0 (5)*
C(4)	0·4445 (8)	0·431 (1)	0·296 (1)	5·3 (5)*
C(5)	0·4521 (7)	0·349 (1)	0·3018 (9)	5·1 (5)*
C(6)	0·4381 (7)	0·314 (1)	0·3528 (9)	4·1 (4)*
C(7)	0·4273 (7)	0·381 (1)	0·5181 (8)	3·7 (4)*
C(8)	0·4030 (7)	0·436 (1)	0·5478 (9)	3·9 (4)*
C(9)	0·4229 (7)	0·491 (1)	0·5826 (9)	4·8 (5)*
C(10)	0·4668 (8)	0·489 (1)	0·592 (1)	5·3 (5)*
C(11)	0·494 (1)	0·435 (2)	0·564 (1)	8·9 (8)*
C(12)	0·473 (1)	0·381 (2)	0·526 (1)	9·6 (9)*
C(13)	0·4243 (6)	0·213 (1)	0·4648 (8)	3·0 (4)*
C(14)	0·4694 (8)	0·193 (1)	0·469 (1)	5·5 (5)*
C(15)	0·4842 (9)	0·113 (2)	0·466 (1)	6·5 (6)*
C(16)	0·4538 (7)	0·051 (1)	0·4564 (9)	4·0 (4)*
C(17)	0·4097 (7)	0·069 (1)	0·4553 (9)	4·6 (5)*
C(18)	0·3940 (7)	0·148 (1)	0·4595 (9)	4·7 (5)*
C(19)	0·3448 (7)	0·312 (1)	0·4714 (8)	3·7 (4)*
C(20)	0·3156 (7)	0·323 (1)	0·4264 (9)	4·8 (5)*
C(21)	0·2702 (8)	0·309 (1)	0·429 (1)	5·4 (5)*
C(22)	0·2524 (9)	0·284 (2)	0·479 (1)	6·5 (6)*
C(23)	0·2785 (8)	0·268 (2)	0·526 (1)	6·5 (6)*
C(24)	0·3243 (7)	0·284 (1)	0·5218 (9)	4·9 (5)*
C(25)	0·1836 (6)	0·568 (1)	0·3189 (8)	2·8 (4)*
C(26)	0·2065 (7)	0·608 (1)	0·3631 (8)	3·7 (4)*
C(27)	0·2183 (7)	0·567 (1)	0·4126 (9)	4·0 (4)*
C(28)	0·2050 (7)	0·486 (1)	0·4184 (9)	4·5 (5)*
C(29)	0·1818 (7)	0·446 (1)	0·3751 (9)	4·6 (5)*
C(30)	0·1727 (7)	0·489 (1)	0·3244 (8)	3·8 (4)*
C(31)	0·1897 (6)	0·723 (1)	0·2582 (8)	3·2 (4)*
C(32)	0·2370 (6)	0·736 (1)	0·2624 (8)	3·7 (4)*
C(33)	0·2518 (7)	0·819 (1)	0·2631 (9)	4·7 (5)*
C(34)	0·2246 (8)	0·883 (1)	0·261 (1)	5·8 (5)*
C(35)	0·1778 (7)	0·870 (1)	0·2568 (9)	4·0 (4)*
C(36)	0·1611 (7)	0·792 (1)	0·2555 (9)	4·1 (4)*
C(37)	0·1073 (6)	0·625 (1)	0·2494 (8)	3·3 (4)*
C(38)	0·0816 (7)	0·597 (1)	0·2959 (9)	4·7 (5)*
C(39)	0·0338 (8)	0·607 (1)	0·292 (1)	5·4 (5)*
C(40)	0·0152 (8)	0·635 (1)	0·244 (1)	5·6 (5)*
C(41)	0·0397 (7)	0·661 (1)	0·1983 (9)	4·5 (5)*
C(42)	0·0881 (7)	0·655 (1)	0·2008 (9)	4·3 (5)*
C(43)	0·1899 (6)	0·569 (1)	0·1924 (8)	3·3 (4)*
C(44)	0·2230 (7)	0·603 (1)	0·160 (1)	5·0 (5)*
C(45)	0·2412 (9)	0·560 (2)	0·113 (1)	7·3 (7)*
C(46)	0·2235 (9)	0·482 (2)	0·100 (1)	6·7 (6)*
C(47)	0·1896 (8)	0·452 (1)	0·134 (1)	5·3 (5)*
C(48)	0·1714 (7)	0·495 (1)	0·1781 (9)	4·5 (5)*
O	0·1085 (7)	0·704 (1)	0·6140 (9)	9·0 (5)*
N	0·1003 (6)	0·573 (1)	0·6170 (8)	5·8 (4)*
C(*S*1)	0·069 (1)	0·504 (2)	0·621 (1)	8·5 (8)*
C(*S*2)	0·147 (1)	0·553 (2)	0·608 (1)	8·3 (8)*
C(*S*3)	0·0813 (9)	0·647 (2)	0·617 (1)	7·2 (7)*

* Atoms were refined isotropically. Anisotropically refined atoms are listed with the isotropic equivalent displacement parameter defined as $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3)]$.

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* Lists of structure factors, atomic coordinates, anisotropic and isotropic thermal parameters of all non-H atoms, and selected bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53801 (47 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. There is only a slight difference, from that used by Adams *et al.* (1989), in the method of synthesis and crystallization of the palladium octatelluride complex. (II) was prepared from $PdCl_2$ and K_2Te_4 in DMF, and precipitated from ethylenediamine, while (I) was prepared from Li_2PdCl_4 and Na_2Te_4 in DMF, and the crystals were formed by diluting the solution with ether. Thus, it is somewhat surprising that two different crystalline forms are obtained. The structure of (I) is composed of Ph_4P^+ cations, $[Pd(Te_4)_2]^{2-}$ anions and DMF molecules. The structures of the Ph_4P^+ cations and DMF molecules are as expected and call for no further comments. The $[Pd(Te_4)_2]^{2-}$ anions occupy general positions and feature a distorted square-planar environment for the palladium. The Te(1) and Te(4) atoms lie 0·68 Å above and below the Te(5)–Pd–Te(8) plane respectively. The $[Pd(Te_4)_2]^{2-}$ anion possesses approximate D_2 symmetry. The structure of $[Pd(Te_4)_2]^{2-}$ is shown in Fig. 1 and is similar to those of $[Ni(S_4)_2]^{2-}$ (Coucouvanis, Patil, Kanatzidis, Detering & Baenziger, 1985; Müller, Krickemeyer, Bögge, Clegg & Sheldrick, 1983) and $[Ni(Se_4)_2]^{2-}$ (Banda, Cusick, Scudder, Craig & Dance, 1989). The $PdTe_4$ five-membered rings are puckered forming an envelope conformation with Te(3) and Te(6) being the unique atoms. The Pd—Te distances and angles in (I) compare reasonably well with those found in the triclinic form (II) (Adams *et al.*, 1989) and are shown in Table 2. Other distances and angles are shown in Table 3. It should be noted that the interligand distances Te(1)—Te(8) and Te(4)—Te(5) are shorter than the corresponding intraligand Te(1)—Te(4) and Te(5)—Te(8) distances. The slight distortion from the ideal square-planar geometry around the Pd atom is probably due to the steric repulsion between the bulky Te_4^{2-} ligands. This distortion, however, is not sufficient to lower the energy of the $x^2 - y^2$ orbital enough and the complex remains diamagnetic in the solid state. As in (II), the Te—Te distances in the Te_4^{2-} ligands show a bond alternation with long Te(1)—Te(2), Te(3)—Te(4), Te(5)—Te(6) and Te(7)—Te(8) bonds and short Te(2)—Te(3) and Te(6)—Te(7) bonds. Other polytellurides showing a similar bond-length alternation are $[MO(Te_4)_2]^{2-}$ (M = Mo, W) (Flomer & Kolis 1989). This bond alternation is common with some transition-metal polychalcogenides and has been attributed to $p_\pi - d_\pi$ M—Te bonding (Ginsberg, Osborne & Sprinkle, 1983).

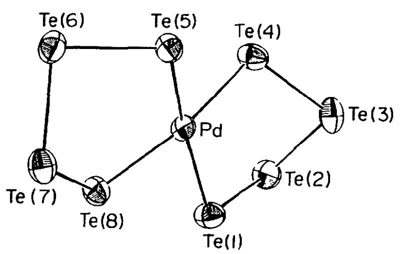

Fig. 1. *ORTEP* representation of the $[Pd(Te_4)_2]^{2-}$ anion with labeling scheme.

Table 2. *Comparison of selected distances* (Å) *and angles* (°) *in the* $[Pd(Te_4)_2]^{2-}$ *anion in* (I) *and* (II) *with e.s.d.'s in parentheses*

	(I)	(II)
Pd—Te(1)	2·589 (2)	2·600 (2)
Pd—Te(4)	2·586 (2)	2·585 (2)
Pd—Te(5)	2·589 (2)	2·603 (2)
Pd—Te(8)	2·584 (2)	2·586 (2)
Pd—Te(mean)*	2·587 (2)	2·593 (8)
Te(1)—Te(2)	2·754 (2)	2·76
Te(2)—Te(3)	2·705 (2)	2·716 (3)
Te(3)—Te(4)	2·764 (2)	2·76
Te(5)—Te(6)	2·768 (2)	2·76
Te(6)—Te(7)	2·695 (2)	2·714 (3)
Te(7)—Te(8)	2·763 (2)	2·76
Te(1)—Pd—Te(4)	103·74 (6)	104·57 (7)
Te(5)—Pd—Te(8)	103·24 (6)	104·59 (8)
Te(1)—Pd—Te(8)	79·09 (6)	76·60 (7)
Te(4)—Pd—Te(5)	78·01 (6)	77·76 (6)

* The e.s.d.'s in the mean bond lengths and the mean bond angles are calculated by the equations $\sigma_1 = [\sum_n (l_n - l)^2/n(n-1)]^{1/2}$, where l_n is the length (or angle) of the nth bond, l the mean length (or angle), n the number of bonds or angles.

Table 3. *Other distances* (Å) *and angles* (°) *in the* $[Pd(Te_4)_2]^{2-}$ *anion in* (I) *with e.s.d.'s in parentheses*

Te(1)···Te(4)	4·071 (3)	Te(4)···Te(5)	3·257 (2)
Te(5)···Te(8)	4·055 (3)	Te(1)···Te(8)	3·294 (2)
Te(4)—Pd—Te(8)	165·02 (8)	Te(1)—Pd—Te(5)	164·6 (1)
Pd—Te(1)—Te(2)	105·34 (6)	Pd—Te(5)—Te(6)	105·27 (6)
Pd—Te(4)—Te(3)	105·43 (6)	Pd—Te(8)—Te(7)	106·13 (7)
Te(1)—Te(2)—Te(3)	94·52 (6)	Te(5)—Te(6)—Te(7)	94·62 (6)
Te(2)—Te(3)—Te(4)	95·28 (6)	Te(6)—Te(7)—Te(8)	94·87 (6)
Te—Te—Te(mean)	94·8 (3)		

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References

Adams, R. D., Wolfe, T. A., Eichhorn, B. W. & Haushalter, R. C. (1989). *Polyhedron*, **8**, 701–703.

Banda, R. M. H., Cusick, J., Scudder, M. L., Craig, D. C. & Dance, I. G. (1989). *Polyhedron*, **8**, 1995–1998.

Coucouvanis, D., Patil, P. R., Kanatzidis, M. G., Detering, B. & Baenziger, N. C. (1985). *Inorg. Chem.* **24**, 24–31.

Eichhorn, B. W. & Haushalter, R. C. (1990). *Inorg. Chem.* **29**, 4084–4085.

Eichhorn, B. W., Haushalter, R. C., Cotton, F. A. & Wilson, B. (1988). *Inorg. Chem.* **27**, 4084–4085.

Flomer, W. A. & Kolis, J. W. (1988). *J. Am. Chem. Soc.* **110**, 3682-3683.

Flomer, W. A. & Kolis, J. W. (1989). *Inorg. Chem.* **28**, 2513–2517.

Flomer, W. A., O'Neal, S. C., Kolis, J. W., Jeter, D. & Cordes, A. W. (1988). *Inorg. Chem.* **27**, 969–971.

Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution.* In *Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi. Delft Univ. Press.

Ginsberg, A. P., Osborne, J. H. & Sprinkle, C. R. (1983). *Inorg. Chem.* **22**, 1781–1790.

Haushalter, R. C. (1985*a*). *Angew. Chem. Int. Ed. Engl.* **24**, 432–433.

Haushalter, R. C. (1985*b*). *Angew. Chem. Int. Ed. Engl.* **24**, 433–435.

Haushalter, R. C. (1985*c*). *Inorg. Chim. Acta*, **102**, L37-L38.

Kanatzidis, M. G. (1988). 196th Am. Chem. Soc. Natl Meet., Los Angeles, Abstract INOR 469.

Müller, A., Krickemeyer, E., Bögge, H., Clegg, W. & Sheldrick G. M. (1983). *Angew. Chem. Int. Ed. Engl.* **22**, 1006–1007.

Sheldrick G. M. (1985). *SHELXS86. Crystallographic Computing* 3; edited by G. M. Sheldrick, C. Krüger & R. Goddard. pp. 175–189. Oxford Univ. Press.

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Structure of [(*R*)-1,2-Dimethoxycarbonylethyl]bis(dimethylglyoximato)-[(*S*)-1-phenylethylamine]cobalt(III)

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Abstract. $C_{22}H_{34}CoN_5O_8$, $M_r = 555{\cdot}5$, trigonal, $P3_2$, $a = 14{\cdot}942\ (2)$, $c = 10{\cdot}174\ (3)$ Å, $V = 1967{\cdot}9\ (7)$ Å^3, $Z = 3$, $D_x = 1{\cdot}407$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 6{\cdot}54$ cm^{-1}, $F(000) = 879$, $T = 298$ K, final $R = 0{\cdot}041$ for 3216 independent reflections. The crystal shows no change on exposure to X-rays at 298 K. The 1,2-dimethoxycarbonylethyl group takes an L-shape conformation.

Introduction. In the serial studies of crystalline-state racemization of bis(dimethylglyoximato)cobalt(III) (cobaloxime) complexes, two kinds of chiral reactive groups bonded to the Co atom [1-cyanoethyl (ce) group, $-C^*H(CH_3)CN$ and 1-methoxycarbonylethyl (mce) group, $-C^*H(CH_3)CO_2CH_3$] have been found to be racemized on exposure to X-rays (Ohashi, 1988; Kurihara, Ohashi, Sasada & Ohgo, 1983; Kurihara, Uchida, Ohashi, Sasada & Ohgo, 1984). Recently it was reported that a cobaloxime complex, with the bulkier chiral group 1,2-dimethoxycarbonylethyl (dmce), was racemized in a cyclohexanone solution and that the racemization rate was not so different from those of the cobaloxime complexes with reactive ce and mce groups (Ohgo, Orisaku, Hasegawa & Takeuchi, 1986). This work was undertaken to ascertain if the crystalline-state racemization is observed for such a bulky chiral group and to determine the structure of the dmce group.

Experimental. The complex was prepared as reported by Ohgo, Orisaku, Hasegawa & Takeuchi (1986). Orange plate-like crystals obtained from an aqueous methanol solution; crystal dimensions 0·5 × 0·5 × 0·5 mm; Rigaku AFC-4 diffractometer with graphite-crystal-monochromated Mo $K\alpha$ radiation; systematic absences $00l$ $l \neq 3n$; cell parameters refined by least-squares method on 15 independent 2θ values with $19 < 2\theta < 27°$; intensity measurement performed up to $2\theta = 55°$; range of hkl: 0 to 10, 0 to 16, -13 to 13; ω–2θ scan technique; scan speed 4° min^{-1}; scan width $(1{\cdot}0 + 0{\cdot}35\tan\theta)°$; background 5 s before and after each scan. Three standard reflections monitored every 100 reflections; no significant variation in intensities; 3381 reflections measured, 3216 with $|F_o| > 3\sigma(F_o)$ considered observed and used for structure determination; corrections for Lorentz and polarization, absorption ignored. Direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and subsequent difference Fourier calculations; full-matrix least squares on F (*SHELX*76; Sheldrick, 1976) with anisotropic thermal parameters for non-H atoms; H atoms derived geometrically (C—H 1·00 Å) and refined with isotropic thermal parameters;

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