implies a weakening of the C(4)—C(5) linkage owing to the proximal C=O bonds. The existence of only two distinct C—C bond types in ca^{2-} [as $(NH_4)_2$-ca.H_2O; 1·401 and 1·535 Å] and in ca^{2-} bridged between bivalent first-row transition-metal ions (Pierpont *et al.*, 1977) implies a delocalization of *p*-quinone π-electron density for which there is no equivalent in [Pd(ca){P(Ph-*m*-CH$_3$)$_3$)$_2$}].

The X-ray crystal structure of [Pd(ca){P(Ph-*m*-CH$_3$)$_3$}$_2$] poses an apparent contradiction with electronic and infrared spectra recently reported for this and related [Pd(ca)(PR_3)$_2$] compounds (Jeong & Holwerda, 1988*a*, 1989*a*). Thus, the title complex exhibits π–π* absorption bands at 344 and 543 cm^{-1}, quite similar in both position and intensity to those of ca^{2-} and Hca$^-$, for which the contribution of the *p*-quinone resonance form cannot be neglected (Jeong & Holwerda, 1989*a*). Similarly, the ca^{2-} contribution to the infrared spectrum of [Pd(ca){P(Ph-*m*-CH$_3$)$_3$}$_2$] [C—O and C=O bands at 1519 and 1643 cm^{-1}, respectively; Jeong & Holwerda (1989*a*)] is virtually indistinguishable from K$_2$ca IR features. The lack of a strong medium dependence of [Pd(π-ca)(PR_3)$_2$] electronic spectra rules out the possibility of a solvent-induced perturbation in the preferred resonance form of coordinated ca^{2-}. Considering that *o*-quinone and *p*-quinone isomers are both consistent with the observed three-line ^{13}C NMR spectrum of coordinated chloranilate in [Pd(ca)(PR_3)$_2$] complexes (Jeong & Holwerda, 1988*a*), it appears likely that resonance forms *B* and *C* contribute to the structure of [Pd(ca){P(Ph-*m*-CH$_3$)$_3$}$_2$] in solution.

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Structure of Bis(1,3-diphenyl-1,3-propanedionato-*O,O'*)(1,2-ethanediamine-*N,N'*)-nickel(II)

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Abstract. $C_{32}H_{30}N_2NiO_4$, $M_r = 565\cdot3$, orthorhombic, $Pna2_1$, $a = 10\cdot347$ (3), $b = 11\cdot586$ (3), $c = 23\cdot694$ (4) Å, $V = 2840$ (1) Å^3, $Z = 4$, $D_x = 1\cdot32$, $D_m = 1\cdot31$ (1) g cm^{-3}, Mo *Kα* radiation, $\lambda = 0\cdot71069$ Å, $\mu = 6\cdot84$ cm^{-1}, $F(000) = 1184$, $T = 293$ (1) K, $R = 0\cdot048$ for 1622 observed reflections with $I \geq 2\cdot5\sigma(I)$. The preparation of a Schiff-base condensate *via* the template reaction of 1,2-ethanediamine and 1,3-

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diphenyl-1,3-propanedione in the presence of nickel-(II) is unsuccessful. A 1:1 adduct is formed by the diamine with the four-coordinate, square-planar nickel bis(β-ketoenolate). The overall geometry is nearly octahedral, with a *cis* configuration of the chelated amines.

Introduction. It has long been known that in addition to undergoing Schiff-base condensation with primary amines, square-planar β-ketoenolates of transition metals form adducts with monodentate and chelating ligands (Hashagen & Fackler, 1965). The arrangement of these ligands in the resulting compound has been investigated by infrared spectroscopy (Marcotrigiano, Battistuzzi & Pellacani, 1972; Izumi, Kurosawa, Kawamoto & Akaiwa, 1975). The geometry about the metal ion becomes octahedral, with monodentate ligands occupying *trans* positions, while bidentate ligands coordinate in a *cis* configuration. However, the recently reported structure of the adduct formed by 1,2-diaminobenzene with bis(1,3-diphenyl-1,3-propanedionato-*O,O'*)nickel(II) (Hotz, Purrington, Singh, Bereman & Sinn, 1987), shows that two diamines act as monodentate ligands and are *trans* to each other in the complex, even though the ligand should be capable of chelating. Also, Schiff-base condensation is not observed, although 2,4-pentanedione readily condenses under the same conditions (L'Eplattenier & Pugin, 1975). The reason for this has been attributed to steric interactions with the bulky β-diketone. In view of the unusual results with 1,2-diaminobenzene, and the limited structural evidence for *cis* coordination (Veidis, Schreiber, Gough & Palenik, 1969), the crystal structure of the 1,2-ethanediamine adduct with the phenyl substituted β-diketone nickel complex, formed in the unsuccessful attempt to synthesize the Schiff-base condensate, was investigated to reveal the geometry adopted by this chelating ligand.

Experimental. The complex was prepared from a 2:2:1 mixture of 1,2-ethanediamine, 1,3-diphenyl-1,3-propanedione and nickel acetate tetrahydrate in refluxing ethanol. The bright green, microcrystalline precipitate was collected by suction filtration. Crystals were grown by slow evaporation from 1:1 ethanol/CH₂Cl₂. Density was measured by flotation in CCl₄/hexanes.

A $0.37 \times 0.26 \times 0.47$ mm block-shaped crystal was mounted on a glass fiber with epoxy resin. Cell dimensions were determined on an Enraf–Nonius CAD-4 diffractometer by accurate centering of 25 reflections with θ in the range 10–15°. Intensity data were collected by the $\omega/2\theta$ method, using monochromated radiation in the range $2 < \theta < 25°$. The intensity of three reflections, chosen as standards, monitored every two hours of exposure time showed

Table 1. *Fractional atom coordinates of non-hydrogen atoms and equivalent isotropic thermal parameters* ($\mathring{A}^2$)

	x	y	z	B_{eq}*
Ni	0.2184 (1)	0.1970 (1)	0.2500 (1)	3.91 (2)
O(1)	0.0971 (6)	0.0752 (6)	0.2168 (6)	4.9 (2)
O(2)	0.3238 (5)	0.2001 (5)	0.1788 (5)	4.3 (2)
O(3)	0.1136 (5)	0.1904 (5)	0.3239 (5)	4.3 (2)
O(4)	0.3386 (5)	0.0731 (5)	0.2836 (5)	4.7 (2)
N(1)	0.1030 (8)	0.3332 (8)	0.2228 (8)	4.8 (2)
N(2)	0.3336 (8)	0.3342 (6)	0.2807 (6)	4.9 (2)
C(1)	0.1178 (9)	0.0207 (8)	0.1710 (8)	4.3 (3)
C(2)	0.2264 (9)	0.0290 (12)	0.1334 (12)	5.8 (5)
C(3)	0.3209 (9)	0.1194 (9)	0.1420 (9)	4.0 (3)
C(4)	0.0160 (9)	-0.0632 (6)	0.1531 (6)	4.4 (3)
C(5)	-0.0095 (10)	-0.0810 (12)	0.0957 (12)	6.2 (4)
C(6)	-0.1087 (12)	-0.1613 (12)	0.0799 (12)	7.8 (5)
C(7)	-0.1757 (13)	-0.2194 (10)	0.1179 (10)	7.4 (5)
C(8)	-0.1503 (13)	-0.2033 (10)	0.1763 (10)	8.3 (5)
C(9)	-0.0502 (10)	-0.1215 (10)	0.1952 (10)	6.1 (4)
C(10)	0.4315 (9)	0.1163 (9)	0.1014 (9)	4.5 (3)
C(11)	0.4922 (12)	0.2233 (12)	0.0874 (12)	6.1 (4)
C(12)	0.6093 (13)	0.2128 (16)	0.0542 (16)	8.7 (6)
C(13)	0.6592 (16)	0.1126 (19)	0.0364 (19)	8.9 (6)
C(14)	0.6023 (13)	0.0121 (16)	0.0516 (16)	8.2 (5)
C(15)	0.4876 (12)	0.0136 (12)	0.0829 (12)	5.8 (4)
C(16)	0.1214 (9)	0.1150 (9)	0.3616 (9)	4.1 (3)
C(17)	0.2230 (9)	0.0377 (9)	0.3661 (9)	3.5 (3)
C(18)	0.3257 (9)	0.0213 (8)	0.3296 (8)	4.1 (3)
C(19)	0.4265 (10)	-0.0649 (9)	0.3438 (9)	5.3 (3)
C(20)	0.4819 (12)	-0.1320 (9)	0.3013 (9)	6.7 (4)
C(21)	0.5814 (15)	-0.2073 (12)	0.3164 (12)	8.2 (5)
C(22)	0.6219 (13)	-0.2185 (10)	0.3704 (10)	8.8 (6)
C(23)	0.5681 (12)	-0.1533 (12)	0.4145 (12)	8.2 (5)
C(24)	0.4691 (10)	-0.0768 (9)	0.4017 (9)	5.7 (4)
C(25)	0.0139 (9)	0.1165 (9)	0.4020 (9)	4.2 (3)
C(26)	-0.0357 (10)	0.0126 (10)	0.4236 (10)	6.2 (4)
C(27)	-0.1515 (12)	0.0149 (15)	0.4561 (15)	7.7 (5)
C(28)	-0.2097 (10)	0.1209 (16)	0.4699 (16)	7.7 (5)
C(29)	-0.1552 (12)	0.2224 (10)	0.4505 (10)	6.0 (4)
C(30)	-0.0475 (9)	0.2194 (9)	0.4178 (9)	5.0 (3)
C(31)	0.1848 (12)	0.4396 (12)	0.2242 (12)	5.6 (3)
C(32)	0.2538 (12)	0.4359 (10)	0.2817 (10)	5.4 (3)

*Equivalent isotropic $B_{eq} = \frac{8}{3}\pi^2(U_{11} + U_{22} + U_{33})$.

only random fluctuations. Intensities of 2857 independent reflections (h 0–12, k 0–13, l 0–28) were measured using a variable scan rate of 0.60–3.5° min^{-1}. During structure solution and refinement, 1622 reflections with $I \geq 2.5\sigma(I)$ were used. Data were corrected for Lorentz and polarization effects, but not for absorption.

Systematic absences $0kl$ $k + l = 2n + 1$, $h0l$ $h = 2n + 1$ indicated either space groups $Pna2_1$ or $Pnam$ (a non-standard setting of $Pnma$). The nickel ion was located by Patterson methods and was constrained to reside at $z = \frac{1}{4}$ (the location of the mirror in $Pnam$) since $Z = 4$. The positions of the remaining non-hydrogen atoms were obtained from subsequent electron density maps, only with the additional phasing of a carefully chosen benzene ring in the non-centrosymmetric space group. The lack of a mirror in the molecule and successful refinement confirmed $Pna2_1$ as the correct space group. The absolute configuration was not determined because refinement assuming both geometries showed no significant effect on the R factor. Refinement was performed on F, using full-matrix least-squares techniques. Initially convergence was achieved at $R = 0.095$ using iso-

Table 2. *Selected bond distances (Å) and angles (°)*

Ni—O(1)	2·046 (7)	C(1)—C(2)	1·44 (2)
Ni—O(2)	2·009 (6)	C(2)—C(3)	1·45 (1)
Ni—O(3)	2·060 (7)	C(16)—C(17)	1·39 (1)
Ni—O(4)	2·059 (7)	C(17)—C(18)	1·38 (1)
Ni—N(1)	2·081 (8)	C(1)—C(4)	1·50 (1)
Ni—N(2)	2·116 (8)	C(3)—C(10)	1·49 (1)
C(1)—O(1)	1·27 (1)	C(16)—C(25)	1·47 (1)
C(3)—O(2)	1·28 (1)	C(18)—C(19)	1·48 (2)
C(16)—O(3)	1·25 (1)	C(31)—N(1)	1·50 (2)
C(18)—O(4)	1·25 (1)	C(32)—N(2)	1·44 (1)
C(31)—C(32)	1·54 (1)		

O(1)—Ni—O(2)	91·3 (3)	Ni—N(2)—C(32)	107·3 (6)
O(1)—Ni—O(3)	88·7 (3)	O(1)—C(1)—C(2)	128·8 (10)
O(1)—Ni—O(4)	92·2 (2)	O(1)—C(1)—C(4)	116·5 (9)
O(1)—Ni—N(1)	93·0 (3)	C(2)—C(1)—C(4)	114·7 (11)
O(2)—Ni—O(4)	90·6 (3)	O(2)—C(3)—C(2)	129·8 (10)
O(2)—Ni—N(1)	92·2 (3)	O(2)—C(3)—C(10)	116·0 (9)
O(2)—Ni—N(2)	88·3 (3)	C(2)—C(3)—C(10)	114·1 (11)
O(3)—Ni—O(4)	87·9 (3)	O(3)—C(16)—C(17)	123·6 (9)
O(3)—Ni—N(1)	89·3 (3)	O(3)—C(16)—C(25)	114·2 (9)
O(3)—Ni—N(2)	91·8 (3)	C(17)—C(16)—C(25)	122·1 (9)
O(4)—Ni—N(2)	92·9 (3)	O(4)—C(18)—C(17)	124·0 (9)
N(1)—Ni—N(2)	82·0 (3)	O(4)—C(18)—C(19)	116·5 (9)
Ni—O(1)—C(1)	124·5 (6)	C(17)—C(18)—C(19)	119·4 (10)
Ni—O(2)—C(3)	123·2 (6)	C(1)—C(2)—C(3)	119·3 (13)
Ni—O(3)—C(16)	126·8 (6)	C(16)—C(17)—C(18)	128·6 (9)
Ni—O(4)—C(18)	127·4 (6)	N(1)—C(31)—C(32)	105·0 (11)
Ni—N(1)—C(31)	107·1 (6)	N(2)—C(32)—C(31)	106·0 (11)

tropic temperature factors. At this point, the atom thermal parameters were allowed to vary anisotropically, resulting in convergence at $R = 0.048$, $wR = 0.051$. A difference map revealed possible hydrogen atoms, but their inclusion had no statistically significant effect on the R factor and thus were not used in the final refinement. In the last cycle of least squares, no atom shifted by more than 0·021 of its e.s.d. and $S = 1.38$. Weights were derived from $w = 1/(\sigma_F^2 + 0.001254F^2)$, where σ_F is from counting statistics. A final difference map was virtually featureless, with $-0.25 \le \Delta\rho \le 0.36$ e Å^{-3}. Scattering factors were taken from Cromer & Mann (1968) and anomalous-dispersion terms were from *International Tables for X-ray Crystallography* (1974). The structure solution program was *SHELX*76 (Sheldrick, 1976). Figures were draw using *ORTEP*II (Johnson, 1976).

Discussion. Atomic parameters are in Table 1 and bond lengths and angles in Table 2.* Atom numbering is shown in Fig. 1, and Fig. 2 is a stereoview of the unit cell.

The structure consists of discrete, neutral molecules. The nickel ion is in a six-coordinate, nearly octahedral, O_4N_2 ligand field. The diamine nitrogens are *cis* to each other. N(1) is *trans* to O(4), N(2) is *trans* to O(1), and O(2) is *trans* to O(3).

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* Lists of structure factors, anisotropic thermal parameters and least-squares-planes data, and a fuller list of bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52966 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The angles about the nickel are all close to 90°, with the exception of the 1,2-ethanediamine chelate [∠N(1)—Ni—N(2)]. The short chain length accounts for the small angle, which is comparable with the angle reported for tris(1,2-ethanediamine)nickel(II) (Caughlan, Mazhar-ul-Haque & Emerson, 1970; Swink & Atoji, 1960). The 1,2-ethanediamine is in the *gauche* configuration [dihedral angle between the N(1)—C(31)—C(32) and N(2)—C(32)—C(31) planes, 63°] which has been observed previously (Wiesner & Lingafelter, 1966).

The two OCCCO chelates show delocalization of the double bonds, in that within each ring, the C—C bonds are of equal length, as are the C—O bonds. Overall, the two rings are similar to each other in orientation and bond twisting, with some differences in individual bond lengths and bond angles. For
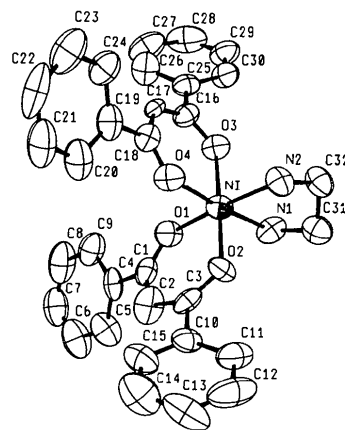

Fig. 1. Perspective view of the molecule showing the numbering of the atoms. Thermal ellipsoids are shown at the 50% probability level.
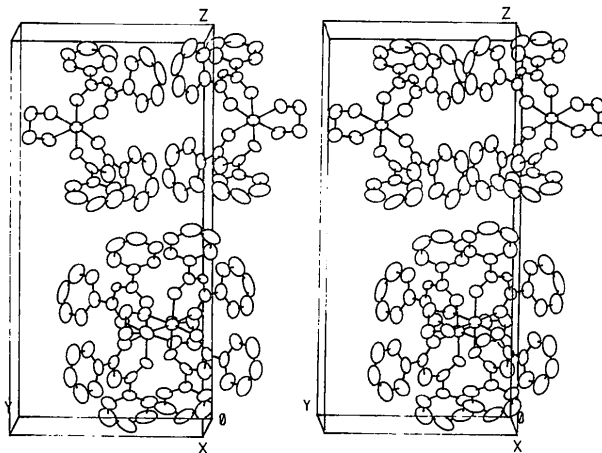

Fig. 2. Stereoview of a unit cell showing molecular packing.

example, the O(1)—Ni—O(2) angle is greater than 90°, while O(3)—Ni—O(4) is less than 90°. This appears to affect the angles about C(1), C(2) and C(3) in one ring and C(16), C(17) and C(18) in the other. However, the dihedral angles that the phenyl rings make with the corresponding chelate ring are close, with 31·1 and 41·5° observed in the β-ketoenolate containing O(1) and O(2), and 36·6 and 42·2° for the other. Rotations reported for other complexes [32·9 and 44·8° (Hotz *et al.*, 1987); 6·5 and 11° (Shugam, Shkol'nikova & Zelentsov, 1966); 5·5 and 8·5° (Knyazeva, Shugam & Shkol'nikova, (1969) and 25·6 and 15·9° (Cornwell & Harrison, 1979)] are not directly comparable because, in these compounds, the two β-diketones are coordinated in a square-planar configuration about the metal ion. In the present compound, the chelates are forced to be closer by the *cis* coordinated 1,2-ethanediamine, making them sterically more crowded. The relatively large rotations observed by Hotz *et al.* (1987) were attributed to steric interactions with the bulky amines in the axial position. However, the fact that the rotations within a chelate ring are different would indicate that crystal packing is also an important contributor. In the free ligand, twists of 3·8 and 16·9° (Williams, 1966) are observed. This structure has been redetermined by X-rays (Hollander, Templeton & Zalkin, 1973) and by neutrons (Jones, 1976). Repulsion between the enolate ring hydrogens and the phenyl groups, and crystal packing were determined to be the major factors which determine the dihedral angle in this compound.

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The *syn* Tetramethylethano-Bridged 3,3′-Di-*tert*-butyltitanocene Dichloride

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Abstract. [1,1′-(2,3-Dimethyl-2,3-butylidene)-3,3′-di-*tert*-butyl-bis-η^5-cyclopenta-1,3-dienyl]titanium dichloride, [Ti(C₂₄H₃₆)]Cl₂, M_r = 443·4, triclinic, $P\bar{1}$, a = 9·8756 (13), b = 10·2758 (11), c = 13·075 (4) Å, α = 75·60 (2), β = 89·87 (2), γ = 66·10 (1)°, V = 1167·7 (5) Å³, Z = 2, D_x = 1·261 g cm⁻³, λ(Mo $K\alpha$) = 0·71073 Å, μ = 5·99 cm⁻¹, $F(000)$ = 472, T = 296 K, R = 0·040 for 3617 data with $I > 3\sigma(I)$. The two Ti—Cl distances are 2·3276 (6) and 2·3597 (6) Å.

The Cl—Ti—Cl angle is 96·35 (3)°. The *tert*-butyl groups splay out from the Cp planes by 11·0°. The Cp centroid–Ti distances are 2·092 and 2·014 Å. The Cp1 centroid–Ti–Cp2 centroid angle is 128·8°. The cyclopentadienyl-ring carbon atoms attached to the (ansa) tetramethylethano bridge exhibit a torsion angle of 36·0 (3)°.

Introduction. Chiral titanocene dichloride derivatives with twofold molecular symmetry can control the stereochemistry of catalytic reactions at the

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