Fig. 2. Stereoview of the packing (viewed down the b direction).

atom with the Cu—O bond distance 2·38 (2) Å. This bond is significantly longer than the equatorial Cu—O bond distances (1·960 and 1·971 Å). The ligand molecule is coordinated in a square-planar manner with slight tetrahedral distortion. The H atom and the methyl group attached to the asymmetric atoms N(1) and N(2) are axial, and are on the same side of the N(1)–N(2)–O(2)–O(1) plane. The atoms C(3) and C(5) near the methyl group, C(4)H₃, are pushed out of the said best plane toward the opposite side of this methyl group. Thus the six-membered ring containing N(1) and O(1) is squeezed into an unstable twist form, the other two six-membered rings being in stable chair forms.

Both [Cu(N-CH₃bctn)(H₂O)](ClO₄)₂.H₂O and [Cu-(ClO₄)(bctn)(H₂O)]ClO₄.H₂O contain three con- secutive six-membered chelate rings. Comparing the crystal structures of these two complexes, we found the following significant results: (1) [Cu(N-CH₃bctn)-(H₂O)](ClO₄)₂.H₂O is monoclinic, while [Cu(ClO₄)-(bctn)(H₂O)]ClO₄.H₂O forms triclinic crystals. (2) For [Cu(N-CH₃bctn)(H₂O)](ClO₄)₂.H₂O, the Cu atom is five-coordinate in a distorted square-pyramidal ge- ometry; for [Cu(ClO₄)(bctn)(H₂O)]ClO₄.H₂O, the Cu atom is six-coordinate in a tetragonally distorted octahedron. (3) For both complexes, the two chiral N centers are in the RS configuration.

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Bis[bis(dimethylphosphinomethyl)methylphosphine]nickel(0)*

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Abstract. [Ni(C₇H₁₉P₃)₂], $M_r = 451·01$, monoclinic, $C2/c$, $a = 17·264$ (2), $b = 8·579$ (1), $c = 17·672$ (1) Å, $\beta = 113·09$ (1)°, $V = 2407·9$ Å³, $Z = 4$, $D_x = 1·24$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1·54178$ Å, $\mu = 49·5$ cm⁻¹, $F(000) = 960$, $T = 294$ K, $wR = 0·051$ for 2079 unique observed structure factors. Two molecules of bis-(dimethylphosphinomethyl)methylphosphine (dmmp) form a molecular complex with nickel(0) by acting as bidentate, chelating ligands to the tetrahedral metal centre. The six-membered MeP(CH₂PMe₂)₂Ni rings adopt a chair conformation. The Ni—P bond lengths are 2·136 (1) and 2·140 (1) Å.

Introduction. Linear triphosphaalkanes of type (I) (R = alkyl, aryl) combine three potential phosphorus donor centres held in close spatial proximity by short, yet flexible, methylene bridges (Appel, Geisler & Schöler, 1979; Karsch, 1982; Hietkamp, Sommer & Stelzer, 1984; Brauer, Hietkamp, Sommer, Stelzer, Müller, Romão & Krüger, 1985). This gives rise to a remarkable potential for, and versatility in, forming transition-metal complexes which has not yet been

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explored in depth. So far, ligands of type (I) could be shown to act as tridentate ligands bridging three metal centres. The trinuclear complexes exhibited either a staggered arrangement of the otherwise unconnected metal centres [(II)] (Brauer *et al.*, 1985) or a nearly linear array with the metal atoms held in place by a second ligand [(III)] (Balch, Fossett, Linehan & Olmstead, 1986). Intermediate between (II) and (III) are complexes where in addition two of the metal centres are connected by a metal—metal bond [(IV)] (Brauer *et al.*, 1985). A chelating complexation mode of (I) has only been reported for one iron complex as yet (Karsch & Neugebauer, 1982), although ligands of type (I) should be ideal chelating ligands by providing two different sets of donor atoms (A/A, A/B) with characteristically different ligand bite.

(I)   (II)   (III)

(IV)   (V)   (VI)
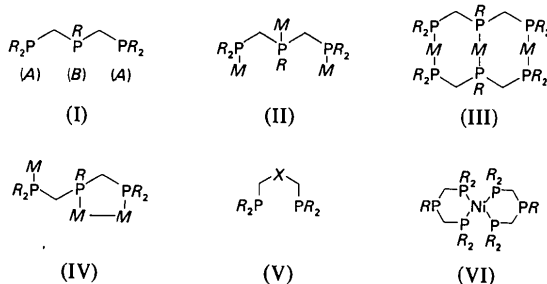
As an extension of our work on complexes of bidentate phosphine ligands (V) (X = AlMe$_2$: Karsch, Appelt & Müller, 1985; X = SiMe$_2$, SnMe$_2$: Karsch & Appelt, 1983; X = ZrCp$_2$: Karsch, Müller & Krüger, 1984) we report here the structure of the Ni^0 complex (VI) of (I) (R = Me, dmmp), prepared from the free ligand and Ni(cod)$_2$, cod = cyclooctadiene, in a molar ratio of 2:1 (Karsch, 1983, unpublished).

Experimental. Colourless crystals (0·8 × 0·3 × 0·1 mm) grown from methanol/diethyl ether; Enraf–Nonius CAD-4 diffractometer equipped with an Ni filter; cell dimensions and their e.s.d.'s obtained by least-squares refinement from the Bragg angles of 73 reflections ($15\cdot9 \leq \theta \leq 74\cdot5°$) from various parts of reciprocal space accurately centred on the diffractometer; 5009 measured reflections in triclinic setting [θ–2θ scans, $\Delta\omega = 0\cdot9° + 0\cdot14°$ tanθ, (sinθ/λ)$_{max}$ = 0·629 Å^{-1}, *hkl* range: ±10, ±12, +20]; orientation (every 250 reflections) and intensity control (every 4000 s of X-ray exposure) by means of three standard reflections (322, 00$\bar{6}$, 151) indicating 5% decay during data collection; monoclinic *C*-centred cell indicated by reduced cell calculations and confirmed by transformation of the data set and subsequent merging of equivalent data (R_{int} = 0·03); corrections for background, radiation damage, and Lorentz and polarization effects, to give 2509 unique structure factors of which 2079 with $F_o \geq 4\cdot0\sigma(F_o)$ were deemed

'observed'; empirical absorption correction (*DIFABS*, Walker & Stuart, 1983) after isotropic refinement of all non-H atoms, which reduced the *R* value from 0·144 to 0·097, maximum and minimum corrections: 1·759/ 0·663; solution by Patterson methods and location of remaining atoms by difference Fourier syntheses; 17 H atoms located in difference maps, two calculated at idealized geometrical positions; refinement with anisotropic thermal parameters, H atoms with isotropic thermal parameters (172 refined parameters, full-matrix); function minimized: $\Sigma w(|F_o| - |F_c|)^2$, unobserved reflections not included in refinement; R = 0·042, wR = 0·051, $w = 1/\sigma^2(F_o)$, R = 0·043 for all reflections, S = 2·5; max. shift/e.s.d. in last cycle = 0·06; final difference map qualitatively featureless, max. residual electron density: +0·35/−0·60 e Å^{-3}; further details of the computing procedures and the programs used as described elsewhere (Krüger, Müller, Erker, Dorf & Engel, 1985); scattering factors for neutral, isolated atoms (except for H) from Cromer & Waber (1965), those for H based on a bonded spherical atom model as given by Stewart, Davidson & Simpson (1965), corrections for f' and f'' (Cu $K\alpha$) applied for Ni, P and C atoms (*International Tables for X-ray Crystallography*, 1974).

Discussion. Table 1 contains the final atomic parameters of the non-H atoms; Table 2 summarizes important interatomic distances and angles.† Fig. 1 gives a view of the molecular structure together with the arbitrary numbering scheme used.

In (VI) two dmmp ligands act as bidentate, chelating ligands to a common Ni^0 metal centre. Of the three phosphine groups of dmmp only the terminal ones are engaged in complexation; the internal one has no close metal contact, as there are no other abnormally short intermolecular distances. The Ni^0 spiro centre of the two six-membered rings thus formed is tetrahedrally coordinated with crystallographically imposed C_2 (2) symmetry. The planes Ni, P(2), P(3) and Ni, P(2*), P(3*) form an angle of 88·6 (3)°, close to the 90° value expected for the ideal tetrahedral case. The endo-, and partially also the exocyclic, P—Ni—P angles deviate from the tetrahedral norm. As expected, the endocyclic angles are smaller (by 6°), most probably as a consequence of the ring strain, while the larger exocyclic ones compensate for this. All C—P—C angles are remarkably close to 100° and thus are similar to values observed in 'free' uncomplexed phosphines. The six-membered rings are in a chair conformation. The

† Additional crystal-structure data and tables of observed and calculated structure-factor amplitudes, anisotropic thermal parameters for the non-H atoms and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43617 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

angle of fold at P(2), P(3) [*i.e.* the angle between the planes Ni,P(2),P(3)/P(2),C(2),P(3),C(3)] of 146·1 (3)° indicates a considerable flattening, whereas at C(2), C(3) [117·2 (3)°] it deviates much less from the idealized cyclohexane value. The Ni—P bond lengths [2·136 (1), 2·140 (1) Å] are equal within standard deviations, as are the P—CH_3 and P—CH_2 bonds.

The structure of (VI) shows that triphosphaalkanes of type (I) can be accommodated relatively strain-free into mononuclear complexes by complexation of the terminal phosphine functions, while the internal one remains uncomplexed. Factors favouring this coordination mode are certainly the sterically non-demanding methyl substituents at the donor centres which also allow for superior donor capabilities of the ligand. Only the observed ring flattening at P(2), P(3) is indicative of some steric strain. It certainly arises from the grossly different C(2)···C(3) and P(2)···P(3) non-bonding distances across the six-membered ring induced by the long Ni—P bonds. An even more pronounced ring

flattening has been observed in the Li^+ complex of the related ligand (V), $X = AlMe_2$ (Karsch *et al.,* 1985), where the even longer Li—P bonds lead to an almost planar LiP_2C_2 portion of the ring. Furthermore, it should be noted that in the Ni^0 complex of (V), $X = ZrCp_2$ (Karsch *et al.,* 1984), the Ni—P bond lengths are comparable to (VI) as is the ring flattening at the P atoms. Quite remarkably, in the former Ni complex a ring flattening of about equal magnitude was also observed at the C atoms of the six-membered ring which was attributed to strain induced by the axial methyl and cyclopentadienyl substituents (Karsch *et al.,* 1984). In (VI) the axial position at P(1) is occupied by the phosphorus lone pair which apparently exerts less stereochemical influence.

As regards the Ni—P bond lengths, there exist only a few structure determinations of homoleptic organophosphine nickel complexes for comparison. The above-mentioned Ni^0 complex of (V), $X = ZrCp_2$, features only marginally longer Ni—P bonds. In bis[bis(dicyclohexylphosphino)methane]nickel(0) (Krüger & Tsay, 1972) the Ni—P bonds are part of planar four-membered rings with drastically reduced P—Ni—P angles (77·7, 77·3°) leading to an Ni—P elongation to 2·210 Å. Also in tetrakis(trimethylphosphine)nickel(I) the Ni—P bond lengths are in a similar range (Gleizes, Dartiguenave, Dartiguenave, Galy & Klein, 1977).

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors for the non-H atoms*

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

	x	y	z	$U_{eq}(\text{Å}^2)$
Ni	0·0000	0·4733 (1)	0·2500	0·042
P(1)	−0·2427 (1)	0·5254 (1)	0·1458 (1)	0·066
P(2)	−0·0879 (1)	0·3384 (1)	0·1525 (1)	0·047
P(3)	−0·0788 (1)	0·6180 (1)	0·2884 (1)	0·049
C(1)	−0·3243 (3)	0·6360 (7)	0·0639 (4)	0·097
C(2)	−0·1833 (2)	0·4466 (5)	0·0881 (2)	0·060
C(3)	−0·1738 (2)	0·6874 (4)	0·2032 (2)	0·059
C(4)	−0·1356 (2)	0·1641 (5)	0·1756 (3)	0·074
C(5)	−0·0582 (3)	0·2545 (7)	0·0714 (3)	0·080
C(6)	−0·0402 (3)	0·8041 (5)	0·3417 (3)	0·074
C(7)	−0·1276 (3)	0·5410 (6)	0·3566 (3)	0·082

Table 2. *Selected bond lengths (Å) and angles (°) including some non-bonded distances*

E.s.d.'s in units of the last significant figure are given in parentheses; symmetry-equivalent atoms are generated from the unique ones by the symmetry operation: $-x, y, 0.5 - z$.

|			
Ni—P(2)	2·136 (1)	P(2)—C(5)	1·847 (5)
Ni—P(3)	2·140 (1)	P(3)—C(3)	1·838 (4)
P(1)—C(1)	1·839 (7)	P(3)—C(6)	1·841 (5)
P(1)—C(2)	1·836 (4)	P(3)—C(7)	1·842 (5)
P(1)—C(3)	1·852 (4)	Ni···P(1)	3·885 (1)
P(2)—C(2)	1·845 (4)	P(2)···P(3)	3·356 (1)
P(2)—C(4)	1·830 (4)	C(2)···C(3)	2·860 (6)
P(3)—Ni—P(2)	103·4 (1)	C(5)—P(2)—C(2)	99·8 (2)
P(3)—Ni—P(3*)	109·1 (1)	C(4)—P(2)—C(2)	100·2 (2)
P(3)—Ni—P(2*)	113·4 (1)	Ni—P(3)—C(7)	120·7 (2)
P(2)—Ni—P(2*)	114·4 (1)	Ni—P(3)—C(6)	121·2 (2)
C(3)—P(1)—C(2)	101·7 (2)	Ni—P(3)—C(3)	113·7 (1)
C(3)—P(1)—C(1)	99·9 (2)	C(7)—P(3)—C(6)	98·3 (2)
C(2)—P(1)—C(1)	100·1 (2)	C(7)—P(3)—C(3)	99·3 (2)
Ni—P(2)—C(5)	120·8 (2)	C(6)—P(3)—C(3)	99·6 (2)
Ni—P(2)—C(4)	120·2 (2)	P(2)—C(2)—P(1)	113·6 (2)
Ni—P(2)—C(2)	113·9 (1)	P(3)—C(3)—P(1)	112·4 (2)
C(5)—P(2)—C(4)	98·1 (2)		
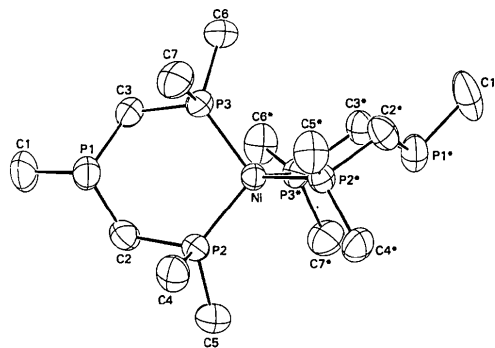
Fig. 1. Perspective view of the molecule with the numbering of atoms (*ORTEP*, Johnson, 1976). Thermal ellipsoids are drawn at the 50% probability level; H atoms are omitted for clarity. Atoms marked with an asterisk are related to those without an asterisk by a crystallographic twofold axis passing through the Ni atom and bisecting the angles P(2)/P(2*) and P(3)/P(3*).

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Structure of a Nickel(II) Perchlorate Complex of a 14-Membered Tetraaza Macrocycle

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Abstract. [Ni(C$_{16}$H$_{36}$N$_4$)](ClO$_4$)$_2$, $M_r = 542 \cdot 10$, monoclinic, $P2_1/a$, $a = 9 \cdot 222$ (7), $b = 14 \cdot 636$ (9), $c = 9 \cdot 670$ (7) Å, $\beta = 114 \cdot 0$ (3)°, $U = 1192 \cdot 3$ Å^3, $Z = 2$, $D_m = 1 \cdot 46$ (2), $D_x = 1 \cdot 51$ g cm^{-3}, λ(Mo $K\alpha$) = $0 \cdot 7107$ Å, $\mu = 19 \cdot 5$ cm^{-1}, $F(000) = 572$, room temperature, final $R = 0 \cdot 070$ for 1179 $[I > 4\sigma(I)]$ independent observed reflections. The structure of the cation [NiL]$^{2+}$, where L is the macrocyclic ligand *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclo-tetradecane, has crystallographically imposed $\bar{1}$ symmetry. The bond lengths and angles of both the cation and the anions are normal. The Ni atom sits in the plane of the four N atoms in the macrocycle [Ni—N $1 \cdot 942$ (6) and $1 \cdot 941$ (9) Å]. The two perchlorate ions are in approximately axial positions but they are each attached to the cation *via* two O···H—N hydrogen bonds [O···N $3 \cdot 07$ (1) and $3 \cdot 09$ (1) Å] rather than *via* Ni···O interactions [Ni···O $3 \cdot 34$ (1) Å].

Introduction. Metal complex cations of the type [ML]$^{n+}$, where L is *C-meso*-5,5,7,12,12,14-hexa-methyl-1-1,4,8,11-tetraazacyclotetradecane, are well known since they were first prepared by Curtis (1964). Structures of the nickel complex cation [NiL]$^{2+}$ have been reported for the acetylacetonate perchlorate by Curtis, Swann & Waters (1973), the chloride by Ito & Toriumi (1981), the fluoride by Toriumi & Ito (1981), and the bromide by Ito, Toriumi & Ito (1981). Both low-spin and high-spin isomers of the bromide and the chloride are known.

Experimental. Orange platelets of the title compound isolated from slow evaporation of an aqueous solution in the presence of an excess of thiourea. Density measured by flotation in CCl$_4$/ligroin. Crystal of approximate size $0 \cdot 2 \times 0 \cdot 4 \times 0 \cdot 4$ mm mounted on Stoe Stadi-2 diffractometer to rotate about the *a* axis. Cell dimensions calculated from 2θ measurement of 20 reflections (2θ range 30 to 40°). Intensity data collected *via* variable-width ω scan, background counts 20 s, step-scan rate $0 \cdot 033°$ s^{-1}, width ($1 \cdot 5 + \sin\mu/\tan\theta$). Absorption and extinction corrections not applied. Standard reflections $h22$ measured every 2θ measurements for each layer; no significant change in intensity. 2082 reflections measured with $2\theta_{max}$ 50°, h 0 to 10, k 0 to 17 and l −10 to 10. 1785 unique reflections, $R_{int} = 0 \cdot 03$. 1179 data with $I > 4\sigma(I)$ used in subsequent calculations.

Structure solved by Patterson method using *SHELX*76 (Sheldrick, 1976) on Amdahl V7A computer. All non-hydrogen atoms refined anisotropically before hydrogen atoms located. Positional and thermal