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Structure of (η-Cyclotriphosphenyl)[1,1,1-tris(diphenylphosphinomethyl)ethane]nickel(II) Triiodide 0·5-Acetone Solvate, $[Ni(C_{41}H_{39}P_3)(P_3)]I_3.0{\cdot}5C_3H_6O$

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Abstract. $M_r = 1186{\cdot}07$, monoclinic, $P2_1/n$, $a = 16{\cdot}763$ (5), $b = 21{\cdot}142$ (7), $c = 13{\cdot}029$ (5) Å, $\beta = 104{\cdot}11$ (5)°, $V = 4478{\cdot}2$ Å^3, $Z = 4$, $D_x = 1{\cdot}76$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 2·72 mm^{-1}, $F(000) = 2312$, $T \sim 293$ K, $R = 0{\cdot}039$ for 3985 reflections. The metal atom in the cation is coordinated by the three P atoms of the phosphine ligand and by the atoms of the cyclic triphosphorus unit. The I—I—I angle in the I_3^- anion is 172·4 (1)° and the I—I distances are 2·908 (1) and 2·963 (1) Å.

Introduction. In the course of an investigation on the reactivity of transition-metal complexes containing trihapto-bonded fifth- and sixth-Group atom rings (Di Vaira, Peruzzini & Stoppioni, 1982), compounds of formula [(triphos)$M(\eta^3$-$P_3)]I_3$ [M = Ni, Pt; triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane] have been obtained by reaction of the corresponding [(triphos)$M(\eta^3$-$P_3)]BF_4$ complexes with I_2. The structure of the Ni derivative [(triphos)Ni(η^3-P_3)]I_3.0·5-$(CH_3)_2CO$ was investigated by X-ray diffraction procedures in order (*a*) to obtain more information on the recently characterized [(triphos)Ni(η^3-P_3)]$^+$ cation (Di Vaira, Sacconi & Stoppioni, 1983) by determining the possible effects on its structure due to changes of the crystalline environment and (*b*) to provide further data on the geometry of the triiodide anion which has attracted considerable interest in past years (Runsink, Swen-Walstra & Migchelsen, 1972, and references cited therein).

Experimental. The complexes [(triphos)$M(\eta^3$-$P_3)]$-I_3.0·5$(CH_3)_2CO$ (M = Ni, Pt) were prepared by concentrating under nitrogen the solution obtained by adding at room temperature I_2 (4 mmol) in ethanol (10 ml) to [(triphos)$M(\eta^3$-$P_3)]BF_4.C_2H_5OH$ (1 mmol) (Di Vaira, Sacconi & Stoppioni, 1983) dissolved in acetone (30 ml). Crystals of the Ni derivative suitable for X-ray investigation obtained by recrystallization of the crude product from acetone and ethanol. Crystal 0·08 × 0·15 × 0·80 mm, transmission factors between 0·65 and 0·83. Philips PW 1100 four-circle automated diffractometer for crystal-data and intensity-data collection. Lattice parameters from least-squares refinement of setting angles of 24 reflections with $16° < \theta < 19°$. θ–2θ scan technique, scan rate 5° min^{-1}, scan width $(1{\cdot}20 + 0{\cdot}30\tan\theta)°$. 6420 reflections ($\pm h$, $+k$, $+l$) measured in the range $1° < \theta < 23°$; three standard reflections monitored every 120 min showed only small oscillations about their mean values (e.s.d.'s <0·01); reflections having $I > 3\sigma(I)$ considered observed and used for structure determination and refinement. Data corrected for Lorentz and polarization factors and for absorption effects. Structure solved from Patterson and Fourier maps and refined by full-matrix least-squares minimizing $\sum w(|F_o| - |F_c|)^2$; $w = 1/\sigma^2(F_o)$. Anisotropic thermal parameters applied to the I, Ni and P atoms and isotropic parameters to the C atoms. H atoms in the cation introduced in calculated positions [riding, C—H = 1·00 Å, $U(H) \simeq 1{\cdot}2U(C)$] except for the methyl H atoms which were refined as part of a rigid CH_3 group. The acetone molecule, lying close to an inversion center, was equally distributed between two symmetry-related orientations; it was assigned a population parameter of 0·5 and an overall temperature factor. With a total of 271 parameters refinement converged at $R = 0{\cdot}039$, $wR = 0{\cdot}039$. Maximum and minimum height in the final difference Fourier synthesis 0·9 and −0·7 e Å^{-3}, respectively; largest shift-to-error ratio in the final refinement cycle 0·09; scattering curves for neutral atoms and anomalous-dispersion correction terms from *International Tables for X-ray Crystallography* (1974); all calculations performed with *SHELX*76 (Sheldrick, 1976).

Discussion. Final atomic parameters are listed in Table 1.* Table 2 shows values of selected bond distances and angles. The structure of the cation is shown in Fig. 1.

The structure consists of [(triphos)Ni(η^3-P_3)]$^+$ cations, I_3^- anions and acetone molecules. The metal atom in the cation is in a six-coordinate environment formed by the three P atoms of the triphos ligand and by the atoms of the cyclic triphosphorus unit. The mean values of the Ni—P(triphos) and Ni—P(P_3) distances, 2·241 (2) and 2·309 (1) Å respectively, agree with those found for the [(triphos)Ni(η^3-P_3)]$BF_4.C_2H_5OH$

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* Anisotropic thermal parameters, H-atom coordinates, detailed bond lengths and angles and structure factor lists have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38616 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final positional parameters* ($\times 10^4$) *and isotropic thermal factors* ($\times 10^3$), *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}/U_{iso}(Å^2)†
I(1)	4488 (1)	3068 (1)	6454 (1)	83 (1)
I(2)	4445 (1)	3337 (1)	4253 (1)	63 (1)
I(3)	4442 (1)	3789 (1)	2099 (1)	76 (1)
Ni	6413 (1)	−408 (1)	3090 (1)	30 (1)
P(1)	7526 (1)	−975 (1)	3004 (1)	32 (1)
P(2)	6730 (1)	428 (1)	2211 (1)	32 (1)
P(3)	7058 (1)	−64 (1)	4704 (1)	32 (1)
P(4)	5053 (1)	−257 (1)	3113 (2)	51 (1)
P(5)	5510 (1)	−1195 (1)	3294 (2)	52 (1)
P(6)	5294 (1)	−746 (1)	1795 (2)	56 (1)
C(1)	8327 (4)	221 (3)	3589 (5)	38 (1)
C(2)	8321 (4)	−391 (3)	2934 (5)	37 (1)
C(3)	7723 (4)	733 (3)	2984 (5)	36 (1)
C(4)	8141 (4)	88 (3)	4684 (5)	37 (1)
C(5)	9196 (4)	511 (3)	3800 (5)	46 (1)
C(11)	7983 (4)	−1509 (3)	4114 (5)	38 (1)
C(12)	8822 (5)	−1549 (4)	4549 (6)	58 (1)
C(13)	9148 (5)	−1988 (4)	5334 (6)	65 (1)
C(14)	8638 (5)	−2391 (4)	5686 (6)	64 (1)
C(15)	7801 (5)	−2368 (4)	5260 (6)	61 (1)
C(16)	7478 (4)	−1915 (4)	4489 (6)	51 (1)
C(21)	7472 (4)	−1520 (3)	1899 (5)	34 (1)
C(22)	8016 (4)	−1499 (3)	1237 (5)	46 (1)
C(23)	7944 (4)	−1951 (4)	438 (6)	56 (1)
C(24)	7356 (4)	−2408 (4)	276 (6)	53 (1)
C(25)	6814 (4)	−2427 (4)	924 (6)	54 (1)
C(26)	6869 (4)	−1981 (3)	1722 (5)	44 (1)
C(31)	6892 (4)	320 (3)	872 (5)	38 (1)
C(32)	6715 (4)	−237 (3)	343 (5)	40 (1)
C(33)	6835 (4)	−295 (4)	−689 (6)	54 (1)
C(34)	7116 (5)	208 (4)	−1162 (7)	63 (1)
C(35)	7295 (5)	764 (4)	−624 (7)	72 (1)
C(36)	7179 (4)	829 (4)	400 (6)	56 (1)
C(41)	6038 (4)	1103 (3)	1963 (5)	35 (1)
C(42)	6213 (4)	1692 (4)	2427 (6)	51 (1)
C(43)	5650 (4)	2176 (4)	2182 (6)	60 (1)
C(44)	4898 (5)	2088 (4)	1448 (6)	59 (1)
C(45)	4725 (5)	1511 (4)	983 (6)	56 (1)
C(46)	5286 (4)	1020 (4)	1234 (5)	47 (1)
C(51)	6728 (4)	677 (3)	5237 (5)	35 (1)
C(52)	6062 (4)	1025 (3)	4683 (6)	44 (1)
C(53)	5847 (4)	1581 (4)	5119 (6)	50 (1)
C(54)	6287 (4)	1789 (4)	6074 (6)	49 (1)
C(55)	6951 (4)	1460 (4)	6628 (6)	52 (1)
C(56)	7171 (4)	898 (3)	6206 (5)	44 (1)
C(61)	7110 (4)	−609 (3)	5813 (5)	35 (1)
C(62)	7841 (4)	−790 (4)	6509 (6)	49 (1)
C(63)	7817 (5)	−1237 (4)	7296 (6)	61 (1)
C(64)	7088 (5)	−1494 (4)	7390 (6)	63 (1)
C(65)	6360 (5)	−1300 (4)	6722 (6)	60 (1)
C(66)	6368 (4)	−859 (4)	5937 (6)	50 (1)
O‡	−735 (7)	−11 (7)	938 (9)	139 (2)
C(71)‡	−298 (7)	−17 (10)	303 (8)	139 (2)
C(72)‡	620 (7)	187 (11)	582 (12)	139 (2)
C(73)‡	−615 (11)	−239 (11)	−862 (8)	139 (2)

† $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$; U_{iso} for C and O atoms.

‡ Atoms of solvent molecule with population parameter 0·5.

compound (Di Vaira, Sacconi & Stoppioni, 1983), 2·243 (4) and 2·306 (5) Å, indicating that the dimensions of the inner skeleton of the complex are substantially unaffected by packing forces. The I_3^- anion is slightly bent and asymmetrical, probably due to the effect of non-bonded interactions in the lattice. There are some contact distances >3·75 Å between the I atoms and nonhydrogen atoms in the acetone molecule or in the cation but no short contacts between I_3^- anions. The mean of the two I—I bond lengths (2·935 Å) is slightly larger than the value expected for the I—I distance (2·920 Å) in the 'free' and symmetrical I_3^- anions (Runsink, Swen-Walstra & Migchelsen, 1972) but is in close agreement with the value of 2·936 Å found for the two independent, both slightly asymmetrical, anions in the structure of $(C_2H_5)_4NI_3$ (Migchelsen & Vos, 1967).

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

I(1)–I(2)	2·908 (1)	Ni–P(5)	2·309 (2)
I(2)–I(3)	2·963 (1)	Ni–P(6)	2·308 (2)
Ni–P(1)	2·244 (2)	P(4)–P(5)	2·120 (3)
Ni–P(2)	2·239 (2)	P(4)–P(6)	2·126 (3)
Ni–P(3)	2·239 (2)	P(5)–P(6)	2·122 (3)
Ni–P(4)	2·309 (2)		
I(1)–I(2)–I(3)	172·4 (1)	P(4)–Ni–P(6)	54·8 (1)
P(1)–Ni–P(2)	95·3 (1)	P(5)–Ni–P(6)	54·7 (1)
P(1)–Ni–P(3)	90·1 (1)	P(4)–P(5)–P(6)	60·1 (1)
P(2)–Ni–P(3)	96·0 (1)	P(5)–P(6)–P(4)	59·9 (1)
P(4)–Ni–P(5)	54·7 (1)	P(6)–P(4)–P(5)	60·0 (1)

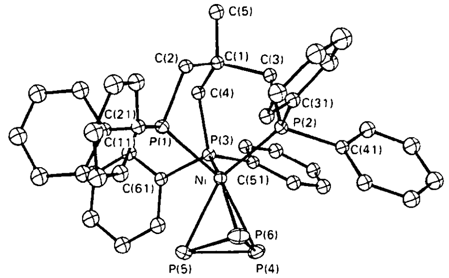

Fig. 1. Perspective view of the $[(\text{triphos})\text{Ni}(\eta^3\text{-P}_3)]^+$ cation. The first C atom of each phenyl group is labeled.

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