

3.174 (1) Å for (1) and Cu(1)—S(1) = 2.926 (1), Cu(2)—S(2) = 2.906 (1) instead of 2.947 (1) and 2.933 (1) Å for (2)]. In this case, one should assume that very small geometrical variations are capable of modifying the electronic state of the Cu^{II} atom to the point of causing a change of colour. Further investigation by electronic spectroscopy will be carried out in order to check this hypothesis.

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Structure of the Dinuclear Platinum Monohydrido Bridged Complex [(PEt₃)₂HPt(μ-H)PtH(PEt₃)₂][BPh₄]

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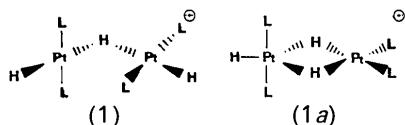
Abstract. (μ-Hydrido)-dihydridotetrakis(triethylphosphine)diplatinum(II) tetraphenylborate, [Pt₂H₃(C₆H₁₅P)₄][B(C₆H₅)₄], *M_r* = 1185.1, monoclinic, *C*2/*n*, *a* = 23.284 (10), *b* = 20.923 (7), *c* = 21.822 (8) Å, β = 93.10 (3)°, *V* = 10 615 (6) Å³, *Z* = 8, *D_x* = 1.483 g cm⁻³, λ(Mo Kα) = 0.71073 Å, μ = 54.7 cm⁻¹, *F*(000) = 4736, *T* = 293 K, *R* = 0.074 for 4646 observed reflections. The structure of the cationic complex consists of two Pt-containing units, which lie on reciprocally perpendicular planes. In each unit, the Pt atom is coordinated in a square-planar arrangement, with one terminal hydride ligand and another hydride ligand, bound to both Pt atoms, in a bridging position.

Introduction. Dinuclear platinum complexes containing one or two bridging H atoms have been widely investigated. Often the hydrido bridges are accompanied by other bridging atoms or groups such as phosphides and carbon monoxide. Among this

type of dinuclear compound, a few trihydridodiplatinum systems have been studied: those containing bridging phosphines [Ph₂PCH₂PPh₂ (Brown, Puddephatt, Rashidi & Seddon, 1977)], chelating phosphines [(*t*-Bu)₂PCH₂CH₂P(*t*-Bu)₂ (Tulip, Yamagata, Yoshida, Wilson, Ibers & Otsuka, 1979) and Ph₂PCH₂CH₂PPh₂ (Minghetti, Bandini, Banditelli & Bonati, 1977; Chiang, Bau, Minghetti, Bandini, Banditelli & Koetzle, 1984)] and monodentate phosphines [PEt₃, PPh₃ and PCy₃ (Bracher, Grove, Pregosin & Venanzi, 1979; Bachechi, Bracher, Grove, Kellenberger, Pregosin, Venanzi & Zambonelli, 1983)].

The X-ray structure of the trihydrido cation [(PEt₃)₂Pt(μ-H)₂PtH(PEt₃)₂]⁺ (1*a*) with two hydrido bridges has already been reported (Bachechi *et al.*, 1983). Its structural isomer, [(PEt₃)₂HPt(μ-H)-PtH(PEt₃)₂]⁺ (1) with a single hydrido bridge could also be prepared and crystallized as the [BPh₄]⁻ salt (Kellenberger, 1982). It readily rearranges in solution

to the dihydrido bridged species and attempts to isolate it from solution have often led to partial or complete formation of the double-bridged isomer (Kellenberger, 1982; Paonessa & Trogler, 1983). Although its crystals rapidly decompose under X-rays, a crystal structure analysis was successfully carried out and is reported here.



Experimental. Crystals were obtained from an acetone-methanol solution in the dark. They decompose easily under X-ray exposure with a gradual change in colour from transparent white to dark brown. They were mounted in a glass capillary tube and so preserved for a longer time. Syntex $P2_1$ computer-controlled diffractometer; graphite-monochromated Mo $K\alpha$ radiation; unit-cell dimensions determined using 15 reflections ($20 \leq 2\theta \leq 26^\circ$); ω -scan mode with 0.8° scan range and scan rate depending on the intensities. The crystals were affected by disorder and two complete sets of diffraction data had to be collected in order to carry out the crystal structure determination. Slightly different conditions were used for each data collection. For the first set of diffraction data one large crystal of dimensions $0.41 \times 0.28 \times 0.80$ mm was used; a total of 8850 reflections were measured in the range $3 \leq 2\theta \leq 40^\circ$. Three standards (022, $24\bar{2}$, 240) measured every 100 reflections showed a gradual decrease in their intensities. Linear correction factors were applied to account for the loss of intensity. Correction for Lorentz and polarization effects. For absorption, an empirical correction was applied, using azimuthal (ψ) scans of three reflections at a high χ angle (88.6 – 91.4°) and with maximum absorption, 32% (North, Phillips & Mathews, 1968). 3200 independent reflections ($R_{\text{int}} = 0.080$) with $I \geq 3\sigma(I)$ were considered observed. Structure solved by Patterson and Fourier methods and refined by least-squares methods to $R = 0.11$. The cationic complex was found to assume three different orientations, one of them prominent (about 90%), and therefore refined, the other two minor and equally populated (about 5%). In the two minor orientations, the Pt_2 units were located midway between the prominent Pt positions (Fig. 1) as often observed in disordered binuclear complexes (Cotton & Powell, 1983; Cotton, Stanley & Walton, 1978). In the prominent orientation the phosphine ligands were in turn affected by a disorder, due to rotation of the ethyl groups around the Pt–P bonds. In the minor orientations only the positions of the Pt atoms appeared on the Fourier maps.

The diffraction data were collected again and three different crystals, selected from a fresh preparation, were used. Crystals of about $0.25 \times 0.20 \times 0.80$ mm were used until the standards revealed a degradation of about 7% of the initial intensity. A total of 12 200 reflections with hkl ranging from $0,0,-25$ to $25,25,25$ up to $2\theta = 56^\circ$ were collected. Each partial collection was separately corrected for the loss of intensities, and also for Lorentz, polarization and shape anisotropy (maximum absorption about 25%), then scaled together and selected according to the condition $I \geq 3\sigma(I)$, obtaining 4646 independent reflections ($R_{\text{int}} = 0.058$). With this new set of data the cationic complex still appeared in three different orientations but the phosphine ligands in the prominent one were not disordered. The refinement included only the Pt atoms of the two minor orientations and was started with occupancy factor ratio (90:0.05:0.05) based on the relative heights of the Pt Fourier peaks. After a few cycles of isotropic refinement ($R = 0.093$), the phenyl rings of the tetraphenylborate anion were treated as rigid groups with H atoms included at calculated positions. Heavier atoms were allowed to vibrate anisotropically, the C atoms of the ethyl groups were maintained isotropic and for the C atoms of the rigid groups only the group thermal parameters were refined. Refinement was carried out on F_o with block-diagonal approximation of the equation matrix. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2$. Convergence reached at $R = 0.074$ ($wR = 0.081$, $S = 7.03$, maximum $\Delta/\sigma = 0.95$). Final difference maps with fluctuations of the electron density in the range from -0.28 to $0.30 \text{ e } \text{Å}^{-3}$. No attempts were made to improve the refinement, since the poor quality of the diffraction data and the complex disorder would not have allowed better results. In spite of this, the sites of the Pt and P atoms appear well determined, but some caution should be used in considering the obtained geometry of the metal core. Scattering factors and anomalous-dispersion terms taken from

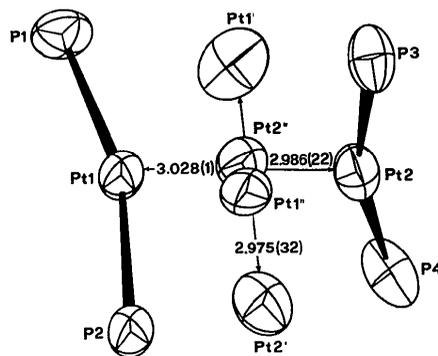


Fig. 1. The disordered core of the cationic complex. The Pt atoms are shown in three differently populated orientations.

International Tables for X-ray Crystallography (1974, Vol. IV). All calculations performed on the HP 21MX computer of the CNR Research Area, using local programs (Cerrini & Spagna, 1977). Final positional parameters are listed in Table 1.*

The infrared spectrum of the complex shows an absorption band at 2140 cm⁻¹ for the terminal hydrides and a broad absorption band between 1800 and 1500 cm⁻¹ indicating the presence of the bridging hydride (Kellenberger, 1982).

The hydride region of the ¹H NMR spectrum is very complex. The spectrum showing the ¹H[³¹P] coupling of the isotomeric complex without ¹⁹⁵Pt presents one doublet for the terminal hydrides (H_t = -8.19 p.p.m.) and one triplet for the bridging hydride (H_b = -6.42 p.p.m.) with ²J_{HH} = 10 Hz. The coupling constants with platinum are ¹J_{PtH} = 1102 Hz and ³J_{PtH} = 121 Hz for the terminal hydrides and ¹J_{PtH} = 527 Hz for the bridging hydride (Kellenberger, 1982).

Discussion. The crystal structure contains discrete tetraphenylborate anions and dinuclear trihydridoplatinum(II) cations, with no short contacts between the atoms of the different ions. The complex cation is shown in Fig. 2. Selected bond distances and angles are presented in Table 2.

The tetraphenylborate anion occurs in this structure with the usual distortions from the ideal geometry. The B—C bond lengths are equivalent and average to 1.69 Å and the bond angles range from 107 to 113°.

The structure of the cation consists of two PtP₂ units which lie in planes almost normal to each other. The dihedral angle between the plane through Pt(1),P(1),P(2) and that through Pt(2),P(3),P(4) is 89°. Both PtP₂ units are almost linear with *trans* P atoms. No attempt was made to locate the hydride ligands in this X-ray analysis but their presence is consistent with the coordination geometry around the two Pt atoms and is supported by IR and NMR evidence. The coordination around the Pt atoms can be described as square-planar with two apparently vacant sites. When these sites are considered occupied by the hydride ligands, one of them, shared between the two Pt atoms, is bridging, the others, bound to Pt(1) and Pt(2), respectively, are terminal. Fig. 2 shows the core of the complex with the hydride ligands at calculated positions. The program *HYDEX* (Orpen, 1980) was used to obtain likely sites

Table 1. Atomic coordinates (× 10⁴) and isotropic thermal parameters with their *e.s.d.*'s in parentheses

$$U_{eq} = (1/6\pi^2) \sum_i \sum_j \beta_{ij} a_i a_j$$

	x	y	z	U _{eq} /U _{iso}
Pt(1)	528.5 (4)	1569.7 (4)	2150.4 (4)	0.0655 (3)
Pt(2)	162.7 (5)	2809.4 (5)	1529.2 (4)	0.0732 (3)
Pt(1')	62 (10)	1838 (11)	1409 (10)	0.089 (3)
Pt(2')	757 (9)	269 (11)	2250 (9)	0.073 (2)
Pt(1'')	927 (7)	2189 (7)	1435 (7)	0.083 (3)
Pt(2'')	-108 (7)	2263 (7)	2184 (8)	0.097 (3)
P(1)	761 (3)	857 (4)	1427 (3)	0.08 (1)
P(2)	399 (3)	2057 (3)	3067 (3)	0.12 (1)
P(3)	-787 (3)	2538 (3)	1392 (3)	0.10 (1)
P(4)	1031 (3)	3301 (4)	1477 (3)	0.08 (1)
B	-2351 (11)	371 (13)	4953 (13)	0.10 (1)
C(1)	1495 (27)	667 (29)	1375 (29)	0.11 (1)
C(2)	1851 (21)	587 (23)	1881 (22)	0.14 (1)
C(3)	853 (39)	1052 (46)	627 (42)	0.13 (2)
C(4)	515 (29)	1238 (34)	371 (30)	0.12 (1)
C(5)	329 (24)	132 (28)	1372 (26)	0.11 (1)
C(6)	62 (25)	-97 (29)	1858 (27)	0.12 (1)
C(7)	1094 (27)	2082 (30)	3546 (28)	0.10 (1)
C(8)	1563 (14)	1785 (15)	3476 (15)	0.12 (1)
C(9)	-12 (28)	1669 (32)	3557 (30)	0.11 (1)
C(10)	-477 (14)	1256 (16)	3426 (14)	0.12 (1)
C(11)	115 (16)	2878 (18)	3108 (17)	0.14 (1)
C(12)	154 (12)	3181 (14)	3734 (13)	0.11 (1)
C(13)	-1297 (20)	2913 (23)	1866 (21)	0.15 (1)
C(14)	-1230 (13)	3504 (16)	2108 (14)	0.11 (1)
C(15)	-1129 (35)	1725 (38)	1413 (36)	0.14 (1)
C(16)	-1222 (28)	1356 (29)	1711 (28)	0.11 (1)
C(17)	-1085 (23)	2774 (26)	630 (25)	0.11 (1)
C(18)	-772 (13)	2698 (15)	92 (14)	0.11 (1)
C(19)	1674 (26)	2934 (29)	1309 (27)	0.11 (1)
C(20)	1907 (30)	2606 (34)	1804 (32)	0.16 (1)
C(21)	1283 (29)	3899 (33)	2093 (32)	0.11 (1)
C(22)	999 (30)	4346 (33)	2107 (32)	0.12 (1)
C(23)	1051 (16)	3851 (19)	813 (18)	0.15 (1)
C(24)	943 (16)	3500 (18)	231 (17)	0.14 (1)
Rigid-group atoms (derived parameters)				
Phenyl ring 1				
C(31)	-2284 (7)	871 (9)	4359 (8)	0.124 (4)
C(32)	-2299 (7)	1525 (10)	4474 (7)	
C(33)	-2199 (8)	1957 (7)	4006 (9)	
C(34)	-2085 (7)	1735 (9)	3424 (8)	
C(35)	-2070 (7)	1080 (10)	3309 (7)	
C(36)	-2170 (7)	649 (7)	3777 (9)	
Phenyl ring 2				
C(37)	-1697 (6)	276 (23)	5310 (8)	0.105 (3)
C(38)	-1633 (6)	50 (21)	5910 (7)	
C(39)	-1086 (8)	-14 (9)	6194 (6)	
C(40)	-603 (6)	148 (23)	5878 (8)	
C(41)	-667 (6)	374 (21)	5278 (7)	
C(42)	-1214 (8)	438 (8)	4995 (6)	
Phenyl ring 3				
C(43)	-2808 (7)	725 (12)	5433 (10)	0.097 (3)
C(44)	-2616 (6)	1012 (16)	5982 (7)	
C(45)	-3003 (7)	1331 (8)	6338 (6)	
C(46)	-3582 (7)	1363 (12)	6146 (6)	
C(47)	-3774 (6)	1076 (16)	5597 (7)	
C(48)	-3387 (7)	757 (8)	5241 (6)	
Phenyl ring 4				
C(49)	-2604 (8)	-357 (7)	4740 (8)	0.119 (4)
C(50)	-3008 (8)	-416 (7)	4249 (8)	
C(51)	-3243 (7)	-1011 (9)	4099 (7)	
C(52)	-3073 (8)	-1548 (7)	4439 (8)	
C(53)	-2670 (8)	-1489 (7)	4931 (8)	
C(54)	-2435 (7)	-894 (9)	5081 (7)	

* Lists of structure factors, anisotropic thermal parameters, rigid group parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55597 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1006]

at potential energy minima. They were then optimized, minimizing the potential energy of the complex.

Table 3 reports the observed Pt—Pt distances in binuclear Pt complexes containing one or two hydrido bridges and one hydrido bridge accompanied by another bridging group. As can be

seen, the Pt—Pt distance in (1) [3.028 (1) Å] is among the longest observed. Only the two closely related complexes [(PEt₃)₂PhPt(μ-H)PtH(PEt₃)₂]⁺ (2) and [(PEt₃)₂PhPt(μ-H)PtPh(PEt₃)₂]⁺ (3), with a single hydride bridge, present Pt—Pt distances longer than in (1). Thus, in all three complexes, the long Pt—Pt distances suggest that the Pt—H—Pt three-centre two-electron bonds have no significant metal—metal direct interaction. In addition, the three Pt—Pt distances are different from each other and display a trend that can be related to the electronic variations which occur when the hydride ligands in (1) are substituted by one or two phenyl ligands as in (2) and (3).

The four Pt—P bond lengths [2.258 (7)–2.288 (7) Å] can be considered equivalent within the high experimental uncertainty and fall below the low end of the range normally observed for alkylphosphine—Pt bonds with phosphorus *trans* to phosphorus (Pidcock, 1981). In the coordination around the Pt atoms, the two P—Pt—P angles [163.1 (3) and 163.9 (2)°] reflect the influence that the bulk of the phosphine ligands exerts upon the ideal square-planar geometry. In both PtP₂ units, the phosphine ligands are strongly and equally bent towards the sites of the terminal hydrides. The twists are only slightly greater than in the symmetrical phenyl-substituted compound (3) [167.6 (2) and 165.9 (2)°], while in the asymmetric phenylhydrido complex, (2), the two P—Pt—P angles are quite different [169.5 (1)° in the PtCP₂ unit and 156.6 (1)° in the PtP₂ unit]. The steric strain among the phosphine ligands is released mainly by a bending towards the terminal hydride.

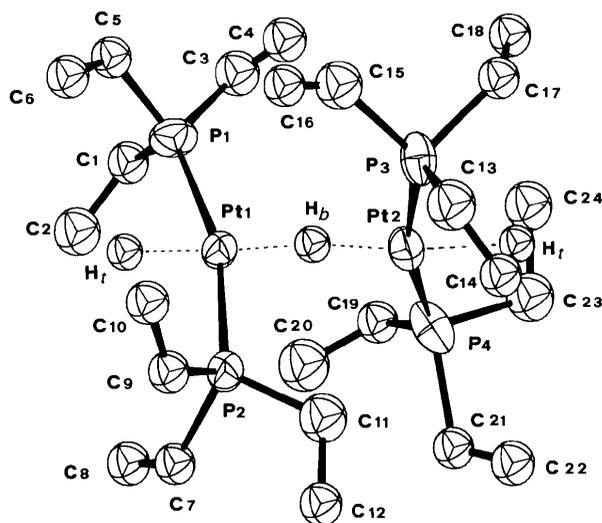


Fig. 2. Perspective view of the cationic complex with ellipsoids at the 30% probability level. The hydride ligands are placed at calculated positions after refinement.

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

Pt(1)—Pt(2)	3.028 (1)	P(4)—C(21)	1.91 (7)
Pt(1)—P(1)	2.258 (7)	P(4)—C(23)	1.85 (4)
Pt(1)—P(2)	2.279 (6)	C(1)—C(2)	1.35 (8)
Pt(2)—P(3)	2.288 (7)	C(3)—C(4)	1.02 (12)
Pt(2)—P(4)	2.277 (8)	C(5)—C(6)	1.35 (8)
P(1)—C(1)	1.76 (6)	C(7)—C(8)	1.27 (7)
P(1)—C(3)	1.82 (9)	C(9)—C(10)	1.40 (8)
P(1)—C(5)	1.82 (6)	C(11)—C(12)	1.51 (5)
P(2)—C(7)	1.88 (6)	C(13)—C(14)	1.35 (6)
P(2)—C(9)	1.68 (7)	C(15)—C(16)	1.04 (10)
P(2)—C(11)	1.81 (4)	C(17)—C(18)	1.42 (6)
P(3)—C(13)	1.80 (5)	C(19)—C(20)	1.37 (9)
P(3)—C(15)	1.88 (8)	C(21)—C(22)	1.15 (10)
P(3)—C(17)	1.84 (6)	C(23)—C(24)	1.48 (6)
P(4)—C(19)	1.74 (6)		
P(1)—Pt(1)—Pt(2)	109.0 (2)	C(13)—P(3)—C(15)	95 (3)
P(2)—Pt(1)—Pt(2)	87.8 (2)	C(13)—P(3)—C(17)	100 (2)
P(1)—Pt(1)—P(2)	163.1 (3)	C(15)—P(3)—C(17)	97 (3)
Pt(1)—Pt(2)—P(3)	95.3 (2)	Pt(2)—Pt(4)—C(19)	126 (2)
Pt(1)—Pt(2)—P(4)	100.4 (2)	Pt(2)—Pt(4)—C(21)	120 (2)
P(3)—Pt(2)—P(4)	163.9 (2)	Pt(2)—Pt(4)—C(23)	112 (1)
Pt(1)—P(1)—C(1)	118 (2)	C(19)—Pt(4)—C(21)	102 (3)
Pt(1)—P(1)—C(3)	125 (3)	C(19)—Pt(4)—C(23)	93 (2)
Pt(1)—P(1)—C(5)	116 (2)	C(21)—Pt(4)—C(23)	97 (2)
C(1)—P(1)—C(3)	80 (4)	P(1)—C(1)—C(2)	122 (4)
C(1)—P(1)—C(5)	110 (3)	P(1)—C(3)—C(4)	119 (8)
C(3)—P(1)—C(5)	103 (4)	P(1)—C(5)—C(6)	121 (5)
Pt(1)—P(2)—C(7)	111 (2)	P(2)—C(7)—C(8)	130 (4)
Pt(1)—P(2)—C(9)	117 (2)	P(2)—C(9)—C(10)	129 (5)
Pt(1)—P(2)—C(11)	122 (1)	P(2)—C(11)—C(12)	117 (2)
C(7)—P(2)—C(9)	99 (3)	P(3)—C(13)—C(14)	124 (3)
C(7)—P(2)—C(11)	102 (2)	P(3)—C(15)—C(16)	142 (7)
C(9)—P(2)—C(11)	104 (3)	P(3)—C(17)—C(18)	122 (4)
Pt(2)—P(3)—C(13)	119 (2)	P(4)—C(19)—C(20)	111 (5)
Pt(2)—P(3)—C(15)	129 (2)	P(4)—C(21)—C(22)	114 (6)
Pt(2)—P(3)—C(17)	112 (2)	P(4)—C(23)—C(24)	111 (3)

Table 3. Pt—Pt distances (Å) in mono- and dihydrido bridged diplatinum complexes

	M...M	H bridges	Reference
Pt(μ-H)Pt			
[(PEt ₃) ₂ PhPt(μ-H)PtPh(PEt ₃) ₂] ⁺	3.238 (1)	1	(a)
[(PEt ₃) ₂ PhPt(μ-H)PtH(PEt ₃) ₂] ⁺	3.093 (1)	1	(b)
[(PEt ₃) ₂ HPt(μ-H)PtH(PEt ₃) ₂] ⁺	3.028 (1)	1	(c)
[(dbpp)HPt(μ-H)PtH(dbpp)] ⁺	2.768 (2)	1	(d)
Pt(μ-H)(μ-L)Pt			
[MePt(μ-H)(μ-dppm) ₂ PtMe] ⁺	2.932 (1)	1	(e)
[(PPh ₃) ₂ PhPt(μ-H)(μ-PPh ₂)Pt(PPh ₃) ₂] ⁺	2.885 (1)	1	(f)
[(L-L)Pt(μ-H)(μ-CO)Pt(L-L)] ⁺	2.790 (1)	1	(g)
[(dppe)Pt(μ-H)(μ-CH ₂ CH ₂)Pt(dppe)] ⁺	2.735 (1)	1	(h)
[(dppe)Pt(μ-H)(μ-CO)Pt(dppe)] ⁺	2.716 (1)	1	(i)
Pt(μ-H)₂Pt			
[(PEt ₃) ₂ HPt(μ-H) ₂ Pt(PEt ₃) ₂] ⁺	2.826 (1)	2	(j)
[(PEt ₃) ₂ PhPt(μ-H) ₂ Pt(PEt ₃) ₂] ⁺	2.819 (1)	2	(j)
[(dppe)HPt(μ-H) ₂ Pt(dppe)] ⁺	2.728 (1)	2	(k)
[(dppe)HPt(μ-H) ₂ Pt(dppe)] [†]	2.711 (1)	2	(l)
[LYPt(μ-H) ₂ PtLY] ⁺	2.692 (3)	2	(m)

Ligand abbreviations: dppm = Ph₂PCH₂PPh₂, dbpp = (*t*-Bu)₂PCH₂CH₂P(*t*-Bu)₂, dppe = Ph₂PCH₂CH₂PPh₂, L-L = Ph₂P({η⁵-C₅H₄})₂Fe)PPh₂, L = P(cyclohexyl), Y = SiMe₃.

References: (a) Carmona, Thouvenot, Venanzi, Bachechi & Zambonelli (1983); (b) Bracher, Grove, Venanzi, Bachechi, Mura & Zambonelli (1978); (c) this work; (d) Tulip, Yamagata, Yoshida, Wilson, Ibers & Otsuka (1979); (e) Brown, Cooper, Frew, Manojlovic-Muir, Muir, Puddephatt & Thomson (1982); (f) Siedle, Newmark & Gleason (1986); (g) Bandini, Banditelli, Cinellu, Sanna, Minghetti, Demartin & Manassero (1989); (h) Minghetti, Albinati, Bandini & Banditelli (1985); (i) Minghetti, Bandini, Banditelli, Bonati, Szostak, Strouse, Knobler & Kaesz (1983); (j) Bachechi, Bracher, Grove, Kellenberger, Pregosin, Venanzi & Zambonelli (1983); (k) Knobler, Kaesz, Minghetti, Bandini, Banditelli & Bonati (1983); (l) Chiang, Bau, Minghetti, Bandini, Banditelli & Koetzle (1984); (m) Ciriano, Green, Howard, Proud, Spencer, Stone & Tsipis (1978).

* Monoclinic modification.

† Triclinic modification.

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Structure of Bis(dimethylammonium) Bis(tetrabutylammonium) β-Octamolybdate

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Abstract. X-ray structure analysis has confirmed the presence of the [Mo₈O₂₆]⁴⁻ anion in [NH₂(CH₃)₂]₂-[N(C₄H₉)₄]₂[Mo₈O₂₆]: monoclinic, *P*₂₁/*c*, *M*_r = 1760.63, *a* = 10.287 (2), *b* = 14.033 (4), *c* = 21.241 (4) Å, β = 99.24 (2)°, *V* = 3026.4 Å³, *Z* = 2, *D*_x = 1.93 g cm⁻³, λ(Mo Kα) = 0.7107 Å, μ = 16.4 cm⁻¹, *F*(000) = 1752, *T* = 294 (1) K, *R* = 0.044, *wR* = 0.069 for 5137 observed reflections. Eight MoO₆ distorted octahedra share edges with short terminal Mo—O bonds (1.694–1.741 Å), bonds of intermediate length (1.889–2.001 Å) and long bonds (2.165–2.465 Å). The structure contains the β-Mo₈O₂₆ polyanion.

Introduction. In previous papers reporting different types of octamolybdate anions (Roman, Gutierrez-

Zorrilla, Martínez-Ripoll & Garcia-Blanco, 1987), it seems that in the solid state the most frequent type is the β-isomer. In a previous paper, we reported that α-[Mo₈O₂₆] was transformed to β-[Mo₈O₂₆] in methanol (Wang, Xu & Wang, 1992). In order to find a mechanism for the isomerization of α- and β-[Mo₈O₂₆]⁴⁻, we continue to study the transformation of α- and β-Mo₈O₂₆. The crystal investigated in this study was grown when trying to prepare a suitable single crystal of triethylammonium octamolybdate from DMF solutions (DMF = *N,N*-dimethylformamide) of the tetrabutylammonium salt. Unexpectedly, crystals of the double salt were obtained. The dimethylammonium ion might have come from the free amine as an impurity in the DMF (DMF was used without subsequent purification). Alternatively, DMF may have been dissociated by water molecules absorbed from the

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