Examination of T_c values for chloride–bromide mixed crystals, which do not have a phase transition (Malliaris & Simopoulos, 1975; DeFotis, Palacio & Carlin, 1979), shows that the extrapolated value for the pure bromide, modification I, is 1·5 K. This is very close to the value we observe in materials crystallized from benzene. This is an indication that between room temperature and helium temperatures the significant intermolecular distances and molecular environments do not change in ways that drastically alter exchange paths observed in the room-temperature data.

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Structure of Bis(1,10-phenanthroline)bis(2,4,6-trinitrophenolato)barium(II) Acetone (1:1), $[Ba(C_{12}H_8N_2)_2(C_6H_2N_3O_7)_2].C_3H_6O$

By R. Postma, J. A. Kanters and A. J. M. Duisenberg

Structural Chemistry Group, University of Utrecht, Padualaan 8, 3508 *TB Utrecht, The Netherlands*

and K. Venkatasubramanian and N. S. Poonia

Chemistry Department, University of Indore, Indore 452-001, *India*

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Abstract. $M_r = 1011{\cdot}98$, orthorhombic, $Pbca$, $a = 18{\cdot}314\,(8)$, $b = 17{\cdot}340\,(4)$, $c = 24{\cdot}629\,(3)$ Å, $V = 7821\,(4)$ Å^3, $Z = 8$, $D_m = 1{\cdot}72$, $D_x = 1{\cdot}72$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo }K\alpha) = 10{\cdot}63$ cm^{-1}, $F(000) = 4048$, $T = 294$ K, $R = 0{\cdot}042$ for 6444 observed reflections. The coordination sphere about Ba consists of four N and four O atoms which form a distorted pentagonal-base trigonal-cap. The two neighbouring phenanthroline molecules act as bidentate ligands through their N atoms, the phenolic O atom and an O atom of an *ortho* nitro group of one of the picrates act as the third bidentate ligand and the coordination is completed by the phenolic O atom of the other picrate and the O atom of the acetone solvate molecule. The angle between the planar phenanthrolines is 60·5 (1)°, that between the picrates is 40·6 (2)°. The benzene rings of both picrates show a similar appreciable distortion from hexagonal symmetry and in both picrates one of the *ortho* nitro groups is severely twisted out of the least-squares plane, 28·6 (2) and 38·9 (2)°, respectively.

Introduction. Complexes of Na$^+$, K$^+$ and Rb$^+$ have been described with a combination of various chelating anionic and neutral ligands such as salicylate, picrate, *o*-nitrophenolate, polyethers and 1,10-phenanthroline (Layton, Nyholm, Banerjee, Fenton, Lestas & Truter, 1970; Truter, 1971; Poonia & Truter, 1973; Poonia, 1975*a*,*b*; Jones, Milburn, Sawyer & Hughes, 1981). In order to study the coordination of alkaline-earth-cation complexes with picrate and 1,10-phenanthroline, the analysis of the title compound was undertaken.

0108-2701/83/091221-05$01.50

Table 1. *Atomic coordinates* ($\times 10^4$; *for* Ba $\times 10^5$, *for* H $\times 10^3$) *and thermal parameters* (Å^2 $\times 10^2$)

Least-squares-derived standard deviations of the least significant figures are given in parentheses.

	x	y	z	U_{eq}*
Ba	43362 (1)	22021 (1)	64835 (1)	3·32 (1)
O(1)	4495 (2)	3653 (2)	6101 (1)	4·52 (1)
O(2)	3235 (2)	4041 (4)	6527 (1)	12·0 (2)
O(3)	2408 (2)	4483 (3)	6045 (2)	9·4 (2)
O(4)	2668 (2)	4982 (3)	4183 (2)	10·3 (2)
O(5)	3629 (2)	4655 (2)	3760 (1)	8·5 (2)
O(6)	5617 (2)	3507 (3)	4717 (1)	8·2 (2)
O(7)	5761 (2)	3833 (2)	5544 (1)	7·3 (1)
N(1)	3026 (2)	4260 (2)	6104 (1)	5·2 (1)
N(2)	3283 (2)	4727 (2)	4174 (2)	6·1 (2)
N(3)	5383 (2)	3762 (2)	5145 (1)	4·6 (1)
C(1)	4233 (2)	3942 (2)	5679 (1)	3·4 (1)
C(2)	3500 (2)	4236 (2)	5628 (1)	3·8 (1)
C(3)	3198 (2)	4496 (2)	5149 (2)	4·5 (1)
C(4)	3614 (2)	4475 (2)	4681 (2)	4·4 (1)
C(5)	4324 (2)	4227 (2)	4689 (2)	4·2 (1)
C(6)	4627 (2)	3998 (2)	5166 (1)	3·7 (1)
H(3)†	273 (2)	474 (2)	517 (2)	
H(5)	457 (2)	422 (2)	433 (2)	
O(8)	4776 (2)	2112 (1)	5427 (1)	5·3 (1)
O(9)	5554 (2)	1270 (2)	6121 (1)	7·5 (1)
O(10)	6037 (3)	245 (2)	5845 (1)	9·8 (2)
O(11)	5998 (2)	− 565 (2)	4012 (1)	6·2 (1)
O(12)	5707 (2)	252 (2)	3384 (1)	7·3 (1)
O(13)	4543 (2)	2670 (2)	3885 (1)	6·6 (1)
O(14)	3871 (2)	2501 (2)	4584 (1)	6·3 (1)
N(4)	5712 (2)	838 (2)	5750 (1)	4·8 (1)
N(5)	5778 (2)	74 (2)	3863 (1)	4·8 (1)
N(6)	4405 (2)	2353 (2)	4315 (2)	4·4 (1)
C(7)	5030 (2)	1665 (2)	5082 (1)	3·7 (1)
C(8)	5498 (2)	1005 (2)	5199 (1)	3·8 (1)
C(9)	5747 (2)	505 (2)	4808 (2)	3·9 (1)
C(10)	5577 (2)	633 (2)	4273 (2)	4·0 (1)
C(11)	5169 (2)	1270 (2)	4115 (2)	4·1 (1)
C(12)	4891 (2)	1747 (2)	4501 (1)	3·7 (1)
H(9)	603 (2)	11 (2)	497 (2)	
H(11)	506 (2)	131 (2)	374 (2)	
N(7)	5590 (2)	2849 (2)	7031 (1)	3·8 (1)
N(8)	5034 (2)	1486 (2)	7430 (1)	4·1 (1)
C(13)	5877 (2)	3506 (2)	6848 (2)	4·4 (1)
C(14)	5854 (2)	2576 (2)	7512 (1)	3·3 (1)
C(15)	6382 (2)	2959 (2)	7819 (1)	4·0 (1)
C(16)	6660 (2)	3658 (2)	7607 (2)	4·8 (1)
C(17)	6416 (2)	3935 (2)	7124 (2)	4·9 (1)
C(18)	6638 (3)	2642 (3)	8314 (2)	5·5 (1)
C(19)	6393 (3)	1959 (3)	8497 (2)	5·4 (1)
C(20)	5844 (2)	1548 (2)	8200 (2)	4·1 (1)
C(21)	5559 (2)	1849 (2)	7714 (1)	3·5 (1)
C(22)	4792 (2)	817 (2)	7621 (2)	5·0 (1)
C(23)	5063 (3)	460 (2)	8090 (2)	5·2 (1)
C(24)	5577 (2)	831 (3)	8384 (2)	5·0 (1)
H(13)	569 (2)	365 (3)	649 (2)	
H(16)	706 (2)	397 (2)	779 (1)	
H(17)	662 (2)	441 (2)	698 (1)	
H(18)	708 (2)	290 (2)	847 (2)	
H(19)	652 (2)	176 (2)	887 (2)	
H(22)	438 (2)	54 (2)	736 (2)	
H(23)	484 (2)	−2 (2)	821 (2)	
H(24)	579 (2)	66 (2)	872 (2)	
N(9)	3839 (2)	2999 (2)	7441 (1)	4·0 (1)
N(10)	3199 (2)	1604 (2)	7198 (1)	4·2 (1)
C(25)	4112 (2)	3686 (2)	7549 (2)	4·8 (1)
C(26)	3338 (2)	2716 (2)	7789 (1)	3·5 (1)
C(27)	3116 (2)	3111 (2)	8259 (1)	4·1 (1)
C(28)	3428 (2)	3838 (2)	8356 (2)	5·0 (1)
C(29)	3927 (2)	4124 (2)	8006 (2)	4·8 (1)
C(30)	2575 (3)	2779 (3)	8607 (2)	5·6 (2)
C(31)	2279 (3)	2096 (3)	8500 (2)	5·8 (2)
C(32)	2487 (2)	1672 (2)	8026 (2)	4·2 (1)
C(33)	3009 (2)	1969 (2)	7665 (1)	3·7 (1)
C(34)	2876 (2)	940 (2)	7089 (2)	4·9 (1)
C(35)	2360 (2)	599 (2)	7420 (2)	5·3 (2)
C(36)	2169 (2)	958 (3)	7896 (2)	5·1 (1)
H(25)	444 (2)	387 (2)	730 (2)	
H(28)	329 (2)	411 (2)	868 (2)	
H(29)	418 (2)	470 (2)	805 (2)	
H(30)	245 (2)	309 (2)	890 (2)	
H(31)	199 (2)	186 (2)	871 (2)	
H(34)	301 (2)	74 (2)	677 (2)	
H(35)	213 (2)	27 (2)	733 (2)	
H(36)	187 (2)	75 (2)	818 (2)	
O(15)	3068 (2)	2373 (2)	5822 (1)	5·7 (1)
C(37)	2688 (2)	2170 (2)	5441 (2)	4·5 (1)
C(38)	2183 (3)	2728 (3)	5167 (2)	6·2 (2)
C(39)	2687 (3)	1372 (3)	5230 (2)	7·0 (2)

* $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

† All H atoms were given a fixed isotropic temperature factor of 0·05 Å^2.

Experimental. Crystals prepared by mixing barium picrate and 1,10-phenanthroline in a 1:2 ratio in a solvent with equal amounts of acetone and methanol; slow evaporation at room temperature yielded yellow crystals, D_m by flotation, rod-shaped crystal, 0·15 × 0·15 × 0·35 mm, 8954 independent intensities, h 0–23, k 0–22, l 0–32, one octant of the reflection sphere ($2\theta_{max} = 55°$), Nonius CAD-4 diffractometer, Zr-filtered Mo $K\alpha$ radiation, $\theta/2\theta$ scan, 6444 $I > 2{\cdot}5\sigma(I)$, lattice parameters from 25 reflections, four periodically measured standard reflections (no significant changes), no corrections for absorption. Patterson and Fourier methods, all H atoms located from difference syntheses and, with the exception of the methyl H atoms, included in the refinement with a constant thermal parameter of 0·05 Å^2, methyl H atoms refined in the rigid-rotation model with fixed C—H distances and H—C—H angles; anisotropic weighted least-squares refinement gave $wR\{=\sum w^{1/2}||F_o|-|F_c||/\sum w^{1/2}F_o\} = 0{\cdot}046$, $w = 1{\cdot}787/[\sigma^2(F_o) + 0{\cdot}001329F_o^2]$, $S = 2{\cdot}62$; refinement of isotropic extinction parameter gave $g = 2{\cdot}6 \times 10^{-8}$, scattering factors from *International Tables for X-ray Crystallography* (1974), anomalous-scattering factors from Cromer & Liberman (1970); final difference synthesis revealed regions of positive and negative electron density of about 1·3 e Å^{-3} at 0·6 Å from Ba, the other features were below the level of ± 0·5 e Å^{-3}, average and maximum shift/error ratios for non-H parameters are 0·01 and 0·19, respectively, for H atoms 0·02 and 1·37, respectively; calculations performed with *SHELX* (Sheldrick, 1976).

Discussion. The atomic coordinates and equivalent isotropic temperature factors are listed in Table 1.* The structure consists of isolated fragments in which Ba coordinates to two picrate ions, two phenanthroline rings and acetone, all belonging to one asymmetric unit. The coordination sphere about Ba consists of four N and four O atoms (Fig. 1). The N atoms are from two adjacent bidentate phenanthrolines, one of the picrates is the third bidentate ligand through an O atom of an

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* Lists of structure factors, anisotropic thermal parameters of the non-H atoms and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38502 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

ortho nitro group and the phenolic O atom, and the eightfold coordination is completed by the phenolic O of the second picrate and O from acetone. The coordination of Ba can be classified as a distorted pentagonal-base trigonal-cap, as is illustrated by Fig. 2, which depicts the trigonal and pentagonal bases of the coordination. The bifurcate angles O(8)—Ba—O(9), N(7)—Ba—N(8) and N(9)—Ba—N(10), involving O and N atoms of the bidentate picrate and phenanthrolines, are nearly equal (Table 2) and their average value of 56·6 (2)° corresponds well with the chelate angles N—Ba—N in the complex [Ba(perchlorate)$_2$-(phenanthroline)$_2$](phenanthroline)$_2$.4H$_2$O [55·1 (5)°] (Smith, O'Reilly, Kennard & White, 1977) and O—K—O in potassium picrate [57·2 (2)°] (Maartmann-Moe, 1969). As was pointed out by Smith, O'Reilly, Kennard & White (1977), the small N—*M*—N angles combined with the relatively large *M*—N distances give rise to nearly trigonal-planar sp^2 bond arrangements about the N donors. The metal–ligand distances involving phenolic O(1) and O(8) are shorter, 2·702 (3) and 2·728 (3) Å, respectively, than those involving O atoms of the nitro group and acetone [O(9) and O(15)] and N atoms of the phenanthrolines [N(7), N(8), N(9) and N(10)], which lie in the narrow range of 2·852 (3)–2·934 (3) Å. These distances compare well with the K—O distances of 2·738 (2) Å for phenolic O and of 2·867 (4), 2·923 (4), 2·789 (4) Å pertaining to O atoms of nitro groups in potassium picrate (Maartmann-Moe, 1969) and the Ba—N distance of 2·956 Å of the phenanthroline complex of Ba(perchlorate)$_2$ (Smith, O'Reilly, Kennard & White, 1977). Corresponding distances and angles of the two picrates and phenanthrolines agree well, the average deviations being 0·011 (11) Å, 0·6 (5)°, and 0·011 (6) Å, 0·4 (3)°, respectively. The benzene rings of the two picrates are distorted in an analogous way. This distortion, which has also been observed in other picrates (Maartmann-Moe, 1969; Thewalt & Bugg, 1972; Palenik, 1972; Jensen, 1975; Herbstein, Kapon & Wielinski, 1977; Dubost, Léger, Hickel & Colleter, 1981; Jones, Milburn, Sawyer & Hughes, 1981), is such that the C—C bonds neighbouring the phenolic C—O bond are lengthened to values of about 1·45 Å which approach those of saturated C(sp^2)—C(sp^2) bonds (Haugen & Trætteberg, 1966), whereas the remaining four C—C bonds are shortened to an average of 1·37 (1) Å, which is well below the value for a normal benzene ring. The variation of the distances is accompanied by a significant change of the bond angles from 120°. The angle between the longer C—C bonds is decreased to about 111° in both picrates, the angles subtended at the *ortho* C atoms are enlarged to about 124° and the three remaining angles have normal values. The distortion has been interpreted as the effect of a major delocalization of the anionic charge (Hough, 1976).

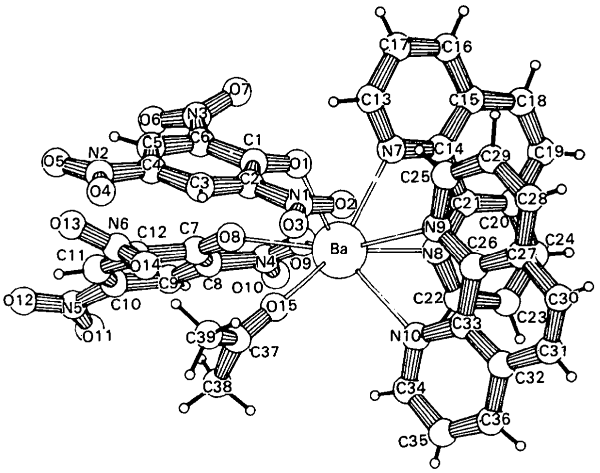

Fig. 1. Molecular conformation and atom numbering.

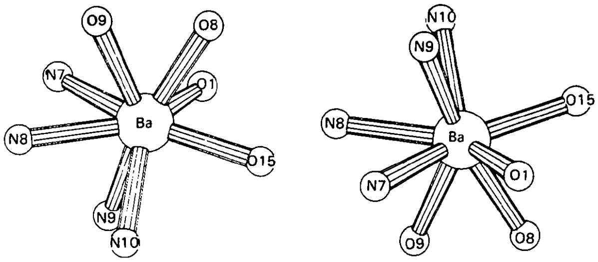

Fig. 2. Ba^{II} coordination showing the pentagonal base (left) and trigonal base (right).

The benzene rings of both picrates are moderately planar [average $\sigma = 0·02$ (1) Å] with the immediate ring substituents showing appreciable deviations from the least-squares planes, their average deviation being 0·06 (3) and 0·09 (3) Å, respectively.* Apart from bending relative to the plane of the benzene ring, the planes of the nitro groups display various degrees of twisting, moderate for one of the *ortho* nitro groups and the *para* nitro group of both picrates [0·4 (2), 5·1 (2)° and 5·9 (2), 14·9 (2)°, respectively], but large for the other *ortho* nitro group [28·6 (2) and 38·9 (2)°, respectively]. The twisting of the nitro groups is also borne out by the pairs of torsion angles between N—O and ring C—C bonds with respect to the N—C bond. The twisting of the *ortho* nitro groups, which is very common in picrates, has been attributed to steric hindrance between the phenolic and nitro-group O atoms (Maartmann-Moe, 1969), though the large twist angle (28°) observed in one of the independent molecules in the structure of 1,3,5-trinitrobenzene (Choi & Abel, 1972) indicates that crystal packing forces must also be taken into account. The phenolic C—O distances are shortened, 1·250 (4) and

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* See deposition footnote.

1·241 (4) Å, respectively, compared with the free acid [1·321 (4) Å, Jensen (1975)], in accordance with a number of observations (Hough, 1976).

Table 2. *Interatomic distances* (Å), *angles* (°) *and selected torsion angles* (°)

Least-squares-derived standard deviations of the least significant figures are given in parentheses.

Ba—O(1)	2·702 (3)	N(5)—C(10)	1·447 (5)	N(9)—C(25)	1·319 (5)
Ba—O(8)	2·728 (3)	N(6)—C(12)	1·451 (5)	N(9)—C(26)	1·348 (5)
Ba—O(9)	2·895 (4)	C(7)—C(8)	1·459 (5)	N(10)—C(33)	1·358 (4)
Ba—O(15)	2·852 (3)	C(7)—C(12)	1·460 (4)	N(10)—C(34)	1·322 (5)
Ba—N(7)	2·889 (3)	C(8)—C(9)	1·374 (5)	C(25)—C(29)	1·399 (6)
Ba—N(8)	2·934 (3)	C(9)—C(10)	1·372 (7)	C(26)—C(27)	1·405 (4)
Ba—N(9)	2·881 (3)	C(10)—C(11)	1·389 (5)	C(26)—C(33)	1·461 (5)
Ba—N(10)	2·917 (3)	C(11)—C(12)	1·359 (5)	C(27)—C(28)	1·405 (5)
		C(9)—H(9)	0·939 (42)	C(27)—C(30)	1·431 (6)
O(1)—C(1)	1·250 (4)	C(11)—H(11)	0·948 (42)	C(28)—C(29)	1·351 (6)
O(2)—N(1)	1·173 (4)			C(30)—C(31)	1·329 (7)
O(3)—N(1)	1·205 (5)	N(7)—C(13)	1·333 (5)	C(31)—C(32)	1·431 (7)
O(4)—N(2)	1·210 (5)	N(7)—C(14)	1·364 (4)	C(32)—C(33)	1·403 (5)
O(5)—N(2)	1·207 (5)	N(8)—C(21)	1·345 (5)	C(32)—C(36)	1·405 (6)
O(6)—N(3)	1·221 (4)	N(8)—C(22)	1·328 (5)	C(34)—C(35)	1·381 (6)
O(7)—N(3)	1·208 (4)	C(13)—C(17)	1·411 (6)	C(35)—C(36)	1·373 (7)
N(1)—C(2)	1·459 (4)	C(14)—C(15)	1·396 (5)	C(25)—H(25)	0·912 (41)
N(2)—C(4)	1·455 (7)	C(14)—C(21)	1·459 (5)	C(28)—H(28)	0·955 (40)
N(3)—C(6)	1·445 (5)	C(15)—C(16)	1·415 (5)	C(29)—H(29)	1·099 (41)
C(1)—C(2)	1·441 (5)	C(15)—C(18)	1·417 (6)	C(30)—H(30)	0·937 (42)
C(1)—C(6)	1·458 (4)	C(16)—C(17)	1·358 (7)	C(31)—H(31)	0·844 (42)
C(2)—C(3)	1·379 (5)	C(18)—C(19)	1·344 (7)	C(34)—H(34)	0·891 (42)
C(3)—C(4)	1·382 (6)	C(19)—C(20)	1·433 (7)	C(35)—H(35)	0·750 (43)
C(4)—C(5)	1·370 (5)	C(20)—C(21)	1·406 (5)	C(36)—H(36)	0·955 (40)
C(5)—C(6)	1·359 (5)	C(20)—C(24)	1·411 (6)		
C(3)—H(3)	0·962 (43)	C(22)—C(23)	1·401 (7)	O(15)—C(37)	1·220 (5)
C(5)—H(5)	0·985 (42)	C(23)—C(24)	1·351 (7)	C(37)—C(38)	1·499 (7)
		C(13)—H(13)	0·983 (40)	C(37)—C(39)	1·478 (6)
O(8)—C(7)	1·241 (4)	C(16)—H(16)	1·012 (40)		
O(9)—N(4)	1·216 (4)	C(17)—H(17)	0·971 (38)		
O(10)—N(4)	1·211 (5)	C(18)—H(18)	0·995 (43)		
O(11)—N(5)	1·235 (5)	C(19)—H(19)	0·996 (40)		
O(12)—N(5)	1·226 (4)	C(22)—H(22)	1·094 (40)		
O(13)—N(6)	1·220 (5)	C(23)—H(23)	0·975 (40)		
O(14)—N(6)	1·209 (5)	C(24)—H(24)	0·967 (43)		
N(4)—C(8)	1·442 (4)				

O(1)—Ba—O(8)	71·9 (1)	O(9)—Ba—N(8)	70·9 (1)
O(1)—Ba—O(9)	109·2 (1)	O(9)—Ba—N(9)	139·8 (1)
O(1)—Ba—N(7)	73·5 (1)	O(9)—Ba—N(10)	122·5 (1)
O(1)—Ba—N(8)	128·6 (1)	O(9)—Ba—O(15)	120·6 (1)
O(1)—Ba—N(9)	82·7 (1)	N(7)—Ba—N(8)	56·5 (1)
O(1)—Ba—N(10)	128·2 (1)	N(7)—Ba—N(9)	71·5 (1)
O(1)—Ba—O(15)	78·0 (1)	N(7)—Ba—N(10)	115·1 (1)
O(8)—Ba—O(9)	56·4 (1)	N(7)—Ba—O(15)	150·8 (1)
O(8)—Ba—N(7)	103·5 (1)	N(8)—Ba—N(9)	72·0 (1)
O(8)—Ba—N(8)	127·2 (1)	N(8)—Ba—N(10)	71·4 (1)
O(8)—Ba—N(9)	154·3 (1)	N(8)—Ba—O(15)	148·5 (1)
O(8)—Ba—N(10)	140·0 (1)	N(9)—Ba—N(10)	56·7 (1)
O(8)—Ba—O(15)	72·6 (1)	N(9)—Ba—O(15)	99·2 (1)
O(9)—Ba—N(7)	75·4 (1)	N(10)—Ba—O(15)	78·5 (1)
O(2)—N(1)—O(3)	121·2 (4)	O(9)—N(4)—O(10)	119·6 (3)
O(2)—N(1)—C(2)	120·7 (4)	O(9)—N(4)—C(8)	121·2 (3)
O(3)—N(1)—C(2)	118·1 (3)	O(10—N(4)—C(8)	119·1 (3)
O(4)—N(2)—O(5)	122·8 (5)	O(11)—N(5)—O(12)	123·1 (3)
O(4)—N(2)—C(4)	118·8 (4)	O(11)—N(5)—C(10)	118·5 (3)
O(5)—N(2)—C(4)	118·4 (4)	O(12)—N(5)—C(10)	118·4 (3)
O(6)—N(3)—O(7)	122·5 (4)	O(13)—N(6)—O(14)	123·2 (4)
O(6)—N(3)—C(6)	118·0 (3)	O(13)—N(6)—C(12)	118·2 (4)
O(7)—N(3)—C(6)	119·4 (3)	O(14)—N(6)—C(12)	118·5 (4)
O(1)—C(1)—C(2)	124·9 (3)	O(8)—C(7)—C(8)	125·1 (3)
O(1)—C(1)—C(6)	123·9 (3)	O(8)—C(7)—C(12)	123·0 (3)
C(2)—C(1)—C(6)	111·2 (2)	C(8)—C(7)—C(12)	111·9 (3)
N(1)—C(2)—C(1)	119·6 (2)	N(4)—C(8)—C(7)	120·2 (3)
N(1)—C(2)—C(3)	116·1 (3)	N(4)—C(8)—C(9)	116·3 (3)
C(1)—C(2)—C(3)	124·3 (3)	C(7)—C(8)—C(9)	123·5 (3)
C(2)—C(3)—C(4)	118·9 (3)	C(8)—C(9)—C(10)	119·7 (3)
N(2)—C(4)—C(3)	118·6 (3)	N(5)—C(10)—C(9)	120·3 (3)
N(2)—C(4)—C(5)	120·1 (4)	N(5)—C(10)—C(11)	118·3 (4)
C(3)—C(4)—C(5)	121·3 (4)	C(9)—C(10)—C(11)	121·3 (4)
C(4)—C(5)—C(6)	119·5 (4)	C(10)—C(11)—C(12)	119·3 (4)
N(3)—C(6)—C(1)	119·1 (3)	N(6)—C(12)—C(7)	119·1 (3)
N(3)—C(6)—C(5)	116·3 (3)	N(6)—C(12)—C(11)	116·7 (3)
C(1)—C(6)—C(5)	124·5 (3)	C(7)—C(12)—C(11)	124·1 (3)
C(14)—C(15)—C(18)	120·7 (3)	C(25)—N(9)—C(26)	117·3 (3)
C(16)—C(15)—C(18)	122·1 (4)	C(33)—N(10)—C(34)	117·6 (3)
C(15)—C(16)—C(17)	120·5 (3)	N(9)—C(25)—C(29)	124·1 (4)
C(13)—C(17)—C(16)	117·8 (4)	N(9)—C(26)—C(27)	122·9 (3)
C(15)—C(18)—C(19)	121·3 (5)	N(9)—C(26)—C(33)	118·1 (3)
C(18)—C(19)—C(20)	120·1 (5)	C(27)—C(26)—C(33)	119·0 (3)
C(19)—C(20)—C(21)	120·7 (4)	C(26)—C(27)—C(28)	117·4 (3)
C(19)—C(20)—C(24)	121·2 (4)	C(26)—C(27)—C(30)	119·8 (3)
C(21)—C(20)—C(24)	118·2 (4)	C(28)—C(27)—C(30)	122·7 (3)
N(8)—C(21)—C(14)	119·4 (3)	C(27)—C(28)—C(29)	119·8 (4)
N(8)—C(21)—C(20)	122·3 (3)	C(25)—C(29)—C(28)	118·5 (3)
C(14)—C(21)—C(20)	118·3 (3)	C(27) C(30) C(31)	121·5 (4)
N(8)—C(22)—C(23)	124·0 (4)	C(30)—C(31)—C(32)	120·7 (5)
C(22)—C(23)—C(24)	118·6 (4)	C(31)—C(32)—C(33)	120·6 (4)
C(20)—C(24)—C(23)	119·3 (4)	C(31)—C(32)—C(36)	121·9 (4)
C(13)—N(7)—C(14)	116·8 (3)	C(33)—C(32)—C(36)	117·5 (4)
C(21)—N(8)—C(22)	117·6 (3)	N(10)—C(33)—C(26)	119·0 (3)
N(7)—C(13)—C(17)	124·3 (4)	N(10)—C(33)—C(32)	122·7 (3)
N(7)—C(14)—C(15)	123·4 (3)	C(26)—C(33)—C(32)	118·3 (3)
N(7)—C(14)—C(21)	117·7 (3)	N(10)—C(34)—C(35)	124·0 (4)
C(15)—C(14)—C(21)	118·9 (3)	C(34)—C(35)—C(36)	119·0 (4)
C(14)—C(15)—C(16)	117·2 (3)	C(32)—C(36)—C(35)	119·2 (4)

O(15)—C(37)—C(38)	120·8 (4)
O(15)—C(37)—C(39)	122·8 (4)
C(38)—C(37)—C(39)	116·4 (4)

O(2)—N(1)—C(2)—C(1)	−0·2 (6)	O(9)—N(4)—C(8)—C(7)	−5·4 (6)
O(2)—N(1)—C(2)—C(3)	179·0 (5)	O(9)—N(4)—C(8)—C(9)	175·8 (4)
O(3)—N(1)—C(2)—C(1)	−177·4 (4)	O(10)—N(4)—C(8)—C(7)	172·5 (4)
O(3)—N(1)—C(2)—C(3)	1·8 (5)	O(10)—N(4)—C(8)—C(9)	−6·3 (6)
O(4)—N(2)—C(4)—C(3)	3·6 (6)	O(11)—N(5)—C(10)—C(9)	11·2 (6)
O(4)—N(2)—C(4)—C(5)	−176·1 (4)	O(11)—N(5)—C(10)—C(11)	−164·6 (4)
O(5)—N(2)—C(4)—C(3)	−174·6 (4)	O(12)—N(5)—C(10)—C(9)	−170·3 (4)
O(5)—N(2)—C(4)—C(5)	5·6 (5)	O(12)—N(5)—C(10)—C(11)	13·9 (5)
O(6)—N(3)—C(6)—C(1)	150·2 (4)	O(13)—N(6)—C(12)—C(7)	144·7 (4)
O(6)—N(3)—C(6)—C(5)	−26·9 (5)	O(13)—N(6)—C(12)—C(11)	−37·6 (5)
O(7)—N(3)—C(6)—C(1)	−30·9 (5)	O(14)—N(6)—C(12)—C(7)	−37·7 (5)
O(7)—N(3)—C(6)—C(5)	152·1 (4)	O(14)—N(6)—C(12)—C(11)	140·0 (4)

The phenanthrolines are approximately planar [$\sigma_{av} = 0{\cdot}04$ (3) and 0·03 (3) Å]; the angle between the planes is 60·5 (1)°, that between the picrates is 40·6 (2)°. The acetone ligand is planar [$\sigma = 0{\cdot}01$ (1) Å] with one methyl group nearly staggered, the other one deviating about 25° from this conformation.

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Structure of Carbonyl-*mer*-trichloro-*trans*-bis(triphenylphosphine)iridium(III),$C_{37}H_{30}Cl_3IrOP_2$

By Francesco Demartin and Norberto Masciocchi

Istituto di Chimica Generale dell'Università, Via G. Venezian 21, 20133 *Milano, Italy*

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Abstract. $M_r = 851\cdot16$, monoclinic, $C2/c$, $a = 24\cdot209$ (3), $b = 9\cdot561$ (2), $c = 22\cdot233$ (3) Å, $\beta = 140\cdot33$ (2)°, $V = 3285$ (2) Å^3, $Z = 4$, $D_m = 1\cdot71$ (2), $D_x = 1\cdot721$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71073$ Å, $\mu(\text{Mo } K\alpha) = 44\cdot2$ cm^{-1}, $F(000) = 1672$, $T = 298$ K, $R = 0\cdot024$ for 2461 independent observed reflections. The X-ray study of the title compound has shown the presence of two triphenylphosphine ligands in *trans* positions, the other ligands lying on the equatorial plane of the coordination octahedron.

Introduction. The title compound was obtained as an unexpected by-product from substitution reactions on $[Ir(CO)_3(PPh_3)]_2$, carried out in chlorinated solvents (Angoletta, Bellon, Demartin & Manassero, 1981; Angoletta, Bellon, Demartin & Sansoni, 1981). The present structural study was undertaken to determine the precise stoichiometry of the new iridium derivative and its stereochemistry.

Experimental. D_m at room temperature by flotation in K_2HgI_4, air-stable yellow prismatic crystal, approximately 0·2 × 0·2 × 0·3 mm, Nonius CAD-4 automatic diffractometer, graphite-monochromatized Mo $K\alpha$, standard CAD-4 centering, indexing and data collection programs, lattice parameters and the orientation matrix refined by least-squares fit of 25 reflections ($8 < \theta < 12°$), 2874 independent reflections, 2θ sphere of 50°, ω scan, $\Delta\omega = 1\cdot5 + 0\cdot35 \tan\theta$, background counted for half of the peak scanning time, h −28–28, k 0–11, l 0–26; three standard reflections revealed no crystal decay; Lorentz, polarization and absorption corrections applied, absorption correction by an empirical method based on a set of φ scans of reflections having χ values near 90° (North, Phillips & Mathews, 1968), maximum and minimum relative transmission factors 1·00 and 0·83; conventional Patterson and Fourier methods, refinement by full-matrix least squares minimizing $\sum w(F_o - |F_c|)^2$, 2461 reflections with $I \geq 3\sigma(I)$, anisotropic thermal parameters for non-hydrogen atoms; contribution of scattering amplitudes of all hydrogen atoms in their expected positions (C—H = 0·95 Å) included in the last cycles of the refinement, with assigned isotropic thermal parameter of 5·00 Å^2, no refinement of hydrogen coordinates attempted; 201 parameters refined, final R and R_w values 0·024 and 0·029 respectively,* $w_{hkl} = 1/\sigma^2(F_o)$, $\sigma(F_o) = \sigma(F_o^2)/2F_o$, $\sigma(F_o^2) = [\sigma^2(I) + (AI)^2]^{\frac{1}{2}}/\text{Lp}$; A, the ignorance factor, is 0·04, maximum shift/e.s.d. = 0·32, maximum peak in final difference Fourier = 1·6 e Å^{-3} (close to Ir); scattering factors and anomalous-dispersion correction from *International Tables for X-ray Crystallography* (1974); all calculations performed on PDP 11/34 using the *Enraf–Nonius Structure Determination Package* (Enraf–Nonius, 1979).

Discussion. Final atomic parameters are given in Table 1; relevant intramolecular distances and angles are reported in Table 2; a view of the molecule of $IrCl_3CO[P(Ph)_3]_2$ and the atomic numbering are shown in Fig. 1.

The molecular structure of the title compound consists of a six-coordinate Ir^{III} ion with octahedral geometry, the two triphenylphosphine ligands being *trans* to each other. The molecule displays C_2 symmetry, with Ir, C, O and Cl(2) atoms lying on a twofold crystallographic axis; however, the idealized symmetry

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38659 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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