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Crystal Structure of a Tetrahedrally Distorted Five-Coordinated Complex of Cobalt(II) with the Ligand Tris(2-diphenylphosphinoethyl)amine

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The crystal structure of the high-spin complex $[Co(np_3)Cl]PF_6$ $[np_3 = N(CH_2CH_2PPh_2)_3]$ has been determined by X-ray photographic techniques, from 2025 observations, and refined by least-squares methods to $R = 0.075$. The unit-cell dimensions are $a = 21.685$ (13), $b = 14.248$ (15), $c = 17.715$ (15) Å, $\beta = 130.13$ (4)°, and $Z = 4$, space group $P2_1/c$. The structure consists of $[Co(np_3)Cl]^+$ and PF_6^- ions. In the complex cation the metal atom is surrounded by one chlorine [Co–Cl = 2.225 (4) Å], three phosphorus [Co–P = 2.37 (1) Å, mean], and one nitrogen atom, that forms a very long bond to the metal [2.675 (10) Å]. The environment formed by the four closest donor atoms is distorted tetrahedral and the nitrogen atom completes a distorted trigonal bipyramid about the metal. The factors responsible for this unusual intermediate coordination are examined.

Introduction

A series of Ni(II) and Co(II) complexes with formula $[M(np_3)X]Y$, where np_3 is the ligand tris(2-diphenylphosphinoethyl)amine, X = Cl, Br, I or NCS, and Y = X, BF_4, PF_6 or BPh_4, has been prepared[1] as a part of a systematic investigation on the geometry and spin-state multiplicity of five-coordinate Ni(II) and Co(II) complexes.[2]

The nickel complexes are all diamagnetic. The cobalt complexes are high spin when X = Cl or Br and are low spin when X = I or NCS, with the single exception of $[Co(np_3)I]BPh_4$, which is high spin in the solid state.[1]

The study of the structure of significant complexes of this series by X-ray analysis has revealed various geometries of coordination, allowed by the considerable flexibility of the tripod ligand. Trigonal-bipyramidal coordination has been found for the nickel complex $[Ni(np_3)I]I$[3] and for $[Ni(np_3)Cl]PF_6$ (preliminary data) and may be safely assigned to all the nickel complexes of this series. Distorted square-pyramidal coordination exists in the low-spin cobalt complex $[Co(np_3)I]I$.[4] On the other hand, in the high-spin cobalt complexes an unusual type of coordination is found, intermediate between four- and five-coordination.

We are reporting here full details on the structure of one of these, $[Co(np_3)Cl]PF_6$, for which a preliminary report has been given.[5]

Crystal Data and Data Collection

Cell constants were obtained from 0*kl* and *h*0*l* Weissenberg photographs with the sodium chloride rotation pattern superimposed for calibration ($a = 5.6273$ Å). Least-squares refinement of 26 2θ values was used. The results are $a = 21.685$ (13), $b = 14.248$ (15), $c = 17.715$ (15) Å, and $\beta = 130.13$ (4)°. A survey of *nkl* and *h*0*l* Weissenberg photographs revealed the systematic absences *h*0*l* for $l = 2n + 1$ and 0*k*0 for $k = 2n + 1$, which are consistent with the space group $P2_1/c$. The calculated density of 1.417 g cm^{-3} for four formula units in the unit cell is in agreement with the observed value of 1.39 g cm^{-3} measured by flotation. The reciprocal lattice levels (0–13)*kl* were collected on a Nonius integrating Weissenberg camera with manganese-filtered Fe Kα radiation (λ 1.9373 Å), using the multiple-film equiinclination technique. The intensities of a total of 2025 reflections were measured on a Nonius microdensitometer. The various levels were put on a common scale by means of *h*0*l* photographs. Two crystals were used to collect levels (0–6)*kl* and, respectively, levels (7–13)*kl*. The crystals were in form of parallelepipeds, elongated along [100], with dimensions 0.50 × 0.25 × 0.18 and 0.55 × 0.20 × 0.16 mm, respectively. No correction for absorption was applied; for μ(Fe Kα) = 59.7 cm^{-1} the maximum and minimum values of the transmission factor within each level differed by about 30%. The reflections 004, 113, 125, 142, $20\bar{4}$, 212, 632, $71\bar{5}$, $81\bar{5}$, $82\bar{5}$ exhibiting large negative ΔF were later considered to be affected by extinction and were omitted from the least-squares refinement. The last four of these, lying on rather high levels, probably suffered in addition from the effect of uncorrected spot elongation. The atomic scattering factors for all atoms except hydrogen were taken from ref 6, that of cobalt being corrected for the real part of the anomalous dispersion according to ref 7, and that of hydrogen was taken from ref 8.

Structure Determination

The position of the heavy atom was provided by a Patterson synthesis. Two subsequent Fourier syntheses yielded the positions of the other nonhydrogen atoms, which were improved with a third Fourier map. Block-diagonal least-squares refinement was then begun, with individual isotropic temperature factors and unit weights and was terminated at an *R* value of 0.122. Unobserved reflections were not included in these or in the following calculations. All the above calculations were performed on an IBM 1620 with programs written by Albano, Bellon, Pompa, and Scatturin.[9] The subsequent full-matrix least-squares refinement and other calculations were performed on the IBM 7090 of CNUCE, Pisa, Italy, using programs written or adapted by Stewart.[10] One isotropic cycle on all atoms was followed by a set of cycles in which anisotropic refinement on atoms heavier than carbon was followed by isotropic refinement on the carbon atoms. Scale factors were not allowed to change during the anisotropic cycles. A difference Fourier calculated at an *R* of 0.080 yielded the positions of 33 of the total 42 independent hydrogen atoms and revealed no other significant features. The hydrogen atoms, in the experimental or calculated position, were introduced in subsequent calculations with temperature factors equal to those of their own carbon atoms and were not refined. When the average shift:error ratio reached values below 0.15, the refinement was terminated. The final *R* and R_w values are 0.075 and 0.101, respectively, R_w being defined as $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. The function minimized in the least-squares calculations was $\Sigma w(|F_o| - |F_c|)^2$ and the weighting scheme adopted during the last cycles was $w = 1$ for reflections with $F_o \leqslant 40$ and $\sqrt{w} = 40/F_o$ for reflections with $F_o > 40$. Final values of the parameters and their estimated standard deviations are reported in Tables I–III. Standard deviations on values of the parameters were calculated by the least-squares program, according to the expression $\sigma_j = [\Sigma w\Delta F^2 a^{jj}/(m - n)]^{1/2}$, where *m* is the number of reflections, *n* the

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Table I. Final Positional (×10^4) and Isotropic Thermal Parameters of Nonhydrogen Atoms with Estimated Standard Deviations in Parentheses

Atom	x/a	y/b	z/c	B, Å^2
Co	2304 (1)	4392 (1)	294 (1)	
Cl	1337 (2)	3475 (2)	−8 (3)	
P(1)	3146 (2)	4742 (2)	2008 (2)	
P(2)	2858 (2)	3520 (2)	−286 (2)	
P(3)	1621 (2)	5755 (2)	−642 (3)	
P(4)	6227 (3)	3742 (3)	2107 (3)	
F(1)	5577 (7)	2983 (9)	1457 (10)	
F(2)	6870 (7)	4506 (8)	2731 (11)	
F(3)	5707 (7)	4109 (8)	2345 (7)	
F(4)	6687 (7)	3038 (9)	2957 (9)	
F(5)	6742 (8)	3409 (9)	1803 (9)	
F(6)	5739 (8)	4382 (10)	1160 (9)	
N	3447 (6)	5521 (6)	637 (7)	
C(1)	4130 (8)	5548 (9)	1705 (9)	4.2 (3)
C(2)	3827 (8)	5693 (9)	2280 (10)	4.3 (3)
C(3)	3724 (9)	5160 (9)	120 (10)	4.7 (3)
C(4)	3796 (9)	4070 (9)	149 (10)	4.9 (3)
C(5)	3129 (9)	6488 (9)	258 (10)	4.8 (3)
C(6)	2282 (9)	6451 (10)	−726 (11)	5.7 (3)
C(7)	2662 (8)	5121 (9)	2477 (9)	4.0 (3)
C(8)	2104 (10)	4574 (11)	2367 (11)	6.0 (4)
C(9)	1692 (11)	4840 (12)	2707 (12)	6.8 (4)
C(10)	1895 (11)	5702 (12)	3213 (12)	7.0 (4)
C(11)	2469 (13)	6250 (14)	3323 (14)	8.4 (5)
C(12)	2855 (10)	5969 (10)	2963 (11)	5.9 (4)
C(13)	3760 (8)	3766 (9)	2786 (9)	3.8 (3)
C(14)	4542 (12)	3879 (14)	3686 (14)	7.8 (5)
C(15)	4991 (14)	3071 (17)	4290 (17)	10.0 (6)
C(16)	4657 (12)	2244 (13)	3958 (14)	7.2 (4)
C(17)	3916 (12)	2079 (13)	3135 (14)	7.7 (5)
C(18)	3465 (10)	2865 (11)	2527 (12)	5.9 (4)
C(19)	3114 (8)	2301 (8)	58 (9)	3.7 (3)
C(20)	2818 (10)	1790 (11)	388 (12)	6.0 (4)
C(21)	3012 (11)	818 (12)	658 (12)	7.0 (4)
C(22)	3549 (10)	435 (11)	569 (11)	5.9 (4)
C(23)	3840 (11)	896 (12)	211 (12)	7.0 (4)
C(24)	3633 (10)	1868 (11)	−50 (12)	6.3 (4)
C(25)	2192 (7)	3472 (8)	−1620 (8)	3.1 (2)
C(26)	2280 (10)	4085 (11)	−2149 (12)	6.6 (4)
C(27)	1726 (12)	4043 (13)	−3202 (14)	7.6 (5)
C(28)	1097 (10)	3374 (11)	−3701 (12)	6.1 (4)
C(29)	1020 (10)	2774 (10)	−3146 (12)	5.8 (4)
C(30)	1585 (9)	2813 (9)	−2113 (10)	4.7 (3)
C(31)	699 (9)	5643 (9)	−1930 (10)	4.4 (3)
C(32)	451 (10)	4777 (11)	−2356 (12)	6.2 (4)
C(33)	−242 (11)	4673 (11)	−3361 (12)	6.5 (4)
C(34)	−625 (12)	5482 (13)	−3867 (14)	7.9 (5)
C(35)	−413 (11)	6331 (13)	−3481 (13)	7.4 (4)
C(36)	279 (10)	6441 (12)	−2471 (12)	6.4 (4)
C(37)	1343 (9)	6495 (9)	−81 (9)	4.0 (3)
C(38)	1591 (10)	7391 (11)	263 (12)	6.3 (4)
C(39)	1343 (12)	7883 (13)	724 (14)	7.8 (5)
C(40)	886 (11)	7455 (13)	839 (13)	7.1 (4)
C(41)	612 (11)	6563 (12)	543 (13)	7.0 (4)
C(42)	858 (10)	6045 (11)	104 (12)	6.1 (4)

number of parameters, and a^{jj} is the jjth element of the inverse least-squares matrix. The factorization of the least-squares matrix due to the separate isotropic and anisotropic refinements performed on different groups of atoms has been accounted for by multiplying the above σ_j values by a suitable factor.[11]

Discussion

The structure of the complex consists of $[Co(np_3)Cl]^+$ cations and of PF_6^- anions. Figure 1 shows a perspective view of the cation, with the labeling of the atoms. Bond distances and angles in the two ions are reported in Tables IV-VI. The coordination about cobalt is of intermediate 4 + 1 type. Four ligands, one chlorine and three phosphorus atoms, form a sort of distorted tetrahedron about the metal and surround it at "normal" bond distances (these are discussed in detail below). The fifth ligand, nitrogen, coordinates from a point outside the face of the tetrahedron defined by the three phosphorus atoms. It forms an unusually long bond to the metal [2.675 (10) Å] so that it could be considered to be semicoordinated.[12] According to an alternative view, which is also of use to the discussion, the coordination can be described as distorted trigonal bipyramidal, with the chlorine and the nitrogen atoms at the apices of the bipyramid (the Cl-Co-N angle measures

Table II. Thermal Parameters (×10^4) for the Atoms Refined Anisotropically,[a] with Estimated Standard Deviations in Parentheses

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	30 (1)	39 (1)	46 (1)	1 (1)	24 (1)	2 (1)
Cl	42 (2)	49 (2)	74 (3)	−11 (1)	36 (2)	−6 (2)
P(1)	31 (2)	37 (2)	49 (2)	−1 (1)	26 (2)	2 (1)
P(2)	28 (2)	41 (2)	45 (2)	1 (1)	22 (2)	−2 (2)
P(3)	27 (2)	44 (2)	59 (2)	7 (1)	26 (2)	13 (2)
P(4)	38 (2)	47 (2)	66 (3)	3 (2)	31 (2)	3 (2)
F(1)	77 (6)	124 (10)	186 (13)	−29 (6)	44 (8)	−68 (9)
F(2)	90 (7)	105 (8)	248 (15)	−59 (6)	92 (9)	−75 (9)
F(3)	81 (6)	169 (10)	109 (8)	7 (7)	65 (7)	−27 (7)
F(4)	75 (6)	166 (11)	153 (11)	23 (7)	46 (7)	115 (9)
F(5)	104 (8)	149 (10)	163 (11)	54 (7)	97 (9)	28 (8)
F(6)	111 (8)	221 (14)	150 (11)	73 (9)	91 (8)	115 (10)
N	45 (6)	40 (6)	73 (8)	2 (5)	45 (6)	4 (6)

[a] Anisotropic thermal factors are of the form $\exp(-\Sigma_{i=1}{}^{3}\Sigma_{j=1}{}^{3} h_ih_j\beta_{ij})$.

Table III. Positional Parameters (×10^3) of Hydrogen Atoms (Numbered According to the Atom to Which They Are Attached)

Atom	x/a	y/b	z/c
H(1a)	430	490	200
H(1b)	450	600	190
H(2a)	445	560	325
H(2b)	325	609	185
H(3a)	430	531	50
H(3b)	339	546	−80
H(4a)	420	368	81
H(4b)	401	410	−25
H(5a)	323	672	85
H(5b)	344	689	20
H(6a)	225	600	−120
H(8)	170	414	180
H(9)	120	452	234
H(10)	150	588	350
H(14)	490	430	378
H(17)	369	140	290
H(20)	235	196	40
H(21)	265	56	90
H(22)	375	−34	65
H(23)	423	70	−5
H(24)	406	232	−20
H(26)	290	464	−179
H(27)	170	458	−370
H(28)	80	330	−455
H(29)	43	230	−340
H(30)	140	260	−175
H(32)	65	408	−200
H(33)	−40	392	−360
H(36)	49	708	−210
H(38)	200	768	9
H(39)	160	860	85
H(41)	20	610	55
H(42)	50	560	−40

[11] A listing of observed and calculated structure factor amplitudes will appear immediately following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1292.

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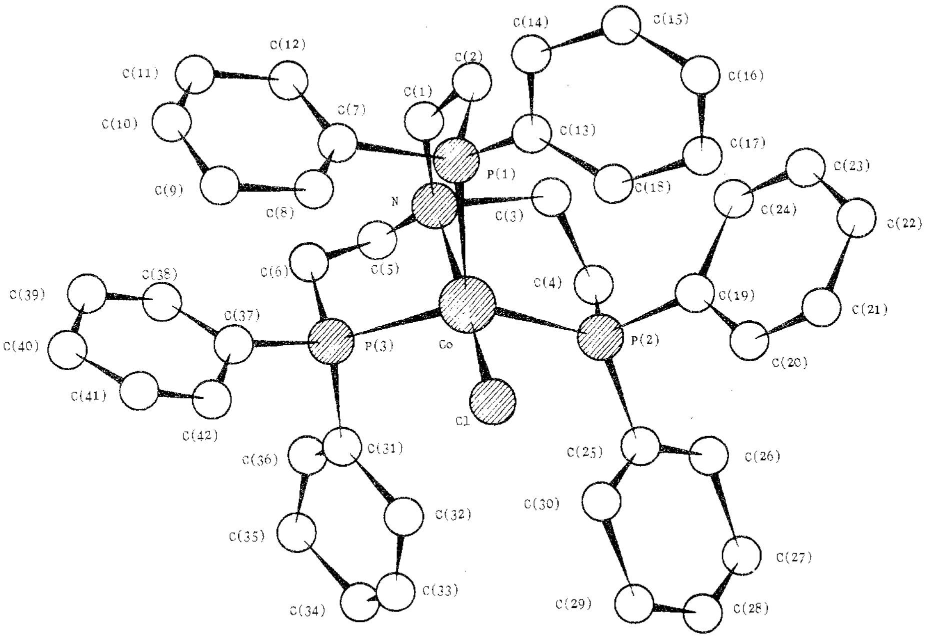

Figure 1. A perspective view of the cation.

Table IV. Distances (Å) and Angles (deg) about the Metal Atom

(a) Distances

Co-Cl	2.225 (4)	Co-P(3)	2.355 (4)
Co-P(1)	2.377 (4)	Co-N	2.675 (10)
Co-P(2)	2.373 (4)		

(b) Angles

Cl-Co-P(1)	105.0 (0.1)	P(1)-Co-P(3)	110.1 (0.1)
Cl-Co-P(2)	104.5 (0.1)	P(2)-Co-P(3)	113.0 (0.1)
Cl-Co-P(3)	104.3 (0.2)	P(1)-Co-N	75.4 (0.2)
Cl-Co-N	178.9 (0.2)	P(2)-Co-N	76.1 (0.2)
P(1)-Co-P(2)	118.4 (0.2)	P(3)-Co-N	74.6 (0.2)

Table V. Distances (Å) and Angles (deg) in the Ligand Molecule

(a) Distances

P(1)-C(2)	1.83 (1)	P(3)-C(37)	1.80 (1)
P(1)-C(7)	1.79 (1)	N-C(1)	1.47 (2)
P(1)-C(13)	1.80 (1)	N-C(3)	1.47 (2)
P(2)-C(4)	1.82 (2)	N-C(5)	1.49 (2)
P(2)-C(19)	1.80 (1)	C(1)-C(2)	1.54 (2)
P(2)-C(25)	1.81 (1)	C(3)-C(4)	1.56 (2)
P(3)-C(6)	1.83 (2)	C(5)-C(6)	1.51 (2)
P(3)-C(31)	1.83 (1)		

(b) Angles

Co-P(1)-C(2)	108.5 (0.4)	C(6)-P(3)-C(31)	103.3 (0.7)
Co-P(1)-C(7)	117.3 (0.5)	C(6)-P(3)-C(37)	106.7 (0.7)
Co-P(1)-C(13)	113.3 (0.4)	C(31)-P(3)-C(37)	104.8 (0.6)
C(2)-P(1)-C(7)	105.7 (0.6)	Co-N-C(1)	109.0 (0.7)
C(2)-P(1)-C(13)	107.3 (0.6)	Co-N-C(3)	109.8 (0.7)
C(7)-P(1)-C(13)	104.1 (0.6)	Co-N-C(5)	111.2 (0.8)
Co-P(2)-C(4)	109.2 (0.5)	C(1)-N-C(3)	109.4 (1.0)
Co-P(2)-C(19)	119.3 (0.4)	C(1)-N-C(5)	110.2 (0.9)
Co-P(2)-C(25)	112.6 (0.4)	C(3)-N-C(5)	107.3 (1.0)
C(4)-P(2)-C(19)	104.7 (0.6)	N-C(1)-C(2)	110.4 (1.1)
C(4)-P(2)-C(25)	107.5 (0.6)	P(1)-C(2)-C(1)	110.1 (0.9)
C(19)-P(2)-C(25)	102.6 (0.5)	N-C(3)-C(4)	113.5 (1.1)
Co-P(3)-C(6)	109.5 (0.5)	P(2)-C(4)-C(3)	110.7 (1.0)
Co-P(3)-C(31)	119.4 (0.4)	N-C(5)-C(6)	110.7 (1.1)
Co-P(3)-C(37)	112.1 (0.4)	P(3)-C(6)-C(5)	111.0 (1.0)

(c) Mean Distances and Angles in the Benzene Rings

Ring	C-C	C-C-C	Ring	C-C	C-C-C
A	1.39 (1)	120.0 (0.8)	D	1.40 (1)	120.0 (0.7)
B	1.38 (1)	120.0 (0.8)	E	1.38 (1)	120.0 (0.8)
C	1.38 (1)	120.0 (0.7)	F	1.38 (1)	120.0 (0.8)

Table VI. Distances (Å) and Angles (deg) in the Anion

Distances

	a	*b*
P(4)-F(1)	1.55 (1)	1.65
P(4)-F(2)	1.54 (1)	1.64
P(4)-F(3)	1.53 (1)	1.59
P(4)-F(4)	1.53 (1)	1.63
P(4)-F(5)	1.59 (1)	1.66
P(4)-F(6)	1.57 (1)	1.68

Angles

F(1)-P(4)-F(2)	178.5 (0.8)	F(2)-P(4)-F(6)	91.7 (0.7)
F(1)-P(4)-F(3)	88.0 (0.7)	F(3)-P(4)-F(4)	94.7 (0.6)
F(1)-P(4)-F(4)	88.8 (0.7)	F(3)-P(4)-F(5)	176.2 (0.7)
F(1)-P(4)-F(5)	92.4 (0.7)	F(3)-P(4)-F(6)	89.2 (0.7)
F(1)-P(4)-F(6)	87.0 (0.7)	F(4)-P(4)-F(5)	89.1 (0.7)
F(2)-P(4)-F(3)	92.8 (0.7)	F(4)-P(4)-F(6)	174.1 (0.7)
F(2)-P(4)-F(4)	92.5 (0.7)	F(5)-P(4)-F(6)	87.0 (0.7)
F(2)-P(4)-F(5)	86.8 (0.7)		

[a] Obtained from final positional parameters. [b] Corrected for thermal shortening.

178.9°). The largest deviation from the idealized trigonal-bipyramidal geometry is due to a considerable shift of the Co-Cl moiety away from the tripod ligand, along the three-fold axis of the bipyramid. The metal atom is thus noticeably depressed (by 0.60 Å) below the equatorial plane of the bipyramid (which is defined by the three phosphorus atoms; the equation of the plane is $17.093x + 8.404y - 6.622z = 8.032$ in monoclinic fractional coordinates) and moves toward a tetrahedral environment as a result of the distortion from five-coordination. Indeed, the angles at the metal, formed by the four closest donor atoms, deviate by only 4.6°, in the mean, from the tetrahedral value, whereas their deviations from values appropriate to a regular trigonal-bipyramidal environment average to 10.4°.

The Co-Cl distance of 2.225 (4) Å approaches the 2.248 (8) Å value found in the complex $[Co(nop_2)Cl]PF_6$,[13] where the ligand molecule [nop_2 = *N,N*-bis(2-diphenylphosphinoethyl)-2-methoxyethylamine] and the geometry of coordination are similar to the present ones. The 2.225 (4) Å value, on the other hand, is well below the range found for typical high-spin five-coordinate Co(II) complexes[14] and is probably even lower than tetrahedral values.[15]

The mean Co-P bond length of 2.37 (1) Å is in partial

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[13] P. Dapporto, G. Fallani, and L. Sacconi, *J. Coord. Chem.*, **1**, 269 (1971).

agreement with the large values found in similar complexes [2.42 Å mean in [Co(nop$_2$)Cl]PF$_6$[13] and 2.43 Å in [Co(n$_2$p$_2$)I]I,[16] where n$_2$p$_2$ = *N*,*N*-bis(2-diphenylphosphinoethyl)-*N*-(2-diethylaminoethyl)amine] and is well above the range established for low-spin five-coordinate complexes.[4,17] Values of cobalt-phosphorus distances in genuinely five-coordinate high-spin complexes of Co(II), which would enable more conclusive comparisons, are not reported and are not expected for a donor set similar to the present one, that favors low-spin for Co(II).[2] It is probably correct to state that, at variance with the Co-Cl bond distance, the Co-P bonds in this complex are longer than would be expected in view of their quasitetrahedral arrangement. Indirect evidence for this is provided by comparison with known nickel-phosphorus distances in tetrahedral complexes of Ni(II)-containing ligands and donor sets similar to the present ones. The 2.28-2.33 Å Ni-P values in ref 18 are lower than the present Co-P value by at least 0.04 Å whereas a difference <0.02 Å would be inferred from comparisons based on strictly similar tetrahedral cases (ref 15b and references therein).

It seems possible to rationalize within the context of the tetrahedral distortion existing in this complex, the peculiar aspects presented by the Co-Cl and Co-P distances, which may be defined "normal" only when contrasted to the very unusual Co-N value. The discussion may also serve to elucidate more general aspects of this coordination.

The short Co-Cl bond length may be due to relatively low repulsive forces exerted on chlorine by the other atoms in the coordination sphere. This in turn should be a result of the tetrahedral distortion and of the rather long Co-P bond distances. Repulsions between electrons in the four bonds, the Co-N and the three Co-P bonds, that crowd together toward one side of the coordination sphere as a result of the tetrahedral distortion, may prevent these bonds and in particular the peripheral (Co-P) bonds formed by the tripod ligand, from shortening to approach tetrahedral values. Presence of the fifth donor, nitrogen, seems essential in this respect, even if the charge distribution in the long Co-N bond may be supposed to approach that of a lone pair localized on nitrogen. Some geometric requirements of the chelating chains of the ligand molecule may also prevent the Co-P bonds from shortening. Factors of this sort cannot be considered determinant for the coordination itself, in view of the well-ascertained flexibility of the ligand molecule; however, they may set rather strict requirements on particular aspects of a given coordination geometry. Indeed, as the comparison with the structure of the complex [Ni(np$_3$)I]I[3] shows, both metal-ligand distances within each chelate ring increase considerably, whereas the angle at the metal decreases, in the course of the tetrahedral distortion. This trend corresponds to that predicted by a recent study,[19] for the simultaneous variation of parameters defining the conformation of five-membered chelate rings. It may be pointed out here that the increase of P···N contact distances and optimization of values of the Co-P-C angles to be considered in subsequent parts of the discussion as further aspects of the tetrahedral distortion also agree with the results of the above conformational study,[19] even though that study was developed for more symmetrical situations than the present one.

Nonbonded interactions due to short contacts between the donor atoms or between other atoms of the ligand molecule definitely do not play any role in determining the Co-P or Co-N bond lengths or the particular mode of chelation. Again, comparison with the trigonal-bipyramidal Ni(II) complex[3] of this series, where the ligand np$_3$ closely approaches the present conformation, shows indeed that all significant contacts are consistently shorter in the nickel complex, which in turn exhibits shorter metal-ligand distances formed by the chelating molecule. In particular, the mean P···P and the above-mentioned P···N distances measure 3.84 and 3.06 Å in [Ni(np$_3$)I]I[3] and increase to the values 3.97 and 3.09 Å in the present complex, respectively.

The very long Co-N distance is typical of this intermediate coordination. It is consistent with the effects of the two factors considered for the cobalt-phosphorus distances. However, it probably constitutes the most evident and direct result of the tetrahedral distortion. The absence of strains indicated by the normal values of distances and angles in the chelating chains of the ligand (Table V) reveals no definite tendency of the nitrogen atom to move closer or farther away from the metal: the cobalt-nitrogen interaction seems to be relatively unimportant to the overall energy balance.

The origin of the very pronounced tetrahedral distortion existing in this complex is certainly to be found in more than one factor. Excluding intramolecular as well as intermolecular contacts (the latter seem to be determinant for the single case of the Co(np$_3$)I chromophore of this series, exhibiting environment-dependent spin state) geometric requirements of the chelating ligand may be considered first.

Comparison with the trigonal-bipyramidal [Ni(np$_3$)I]I[3] shows clearly that major conformational rearrangements in the course of the tetrahedral distortion involve the nearest environment of the phosphorus atoms. In particular, the three M-P-C angles about each phosphorus atom, that deviate by 13.0°, in the mean, from 109° 28′ in the nickel complex, deviate only by 4.4° from that value, in the cobalt complex. Although there is no reason to expect that the environment of phosphorus should be strictly tetrahedral here, evident strains in the M-P-C angles of the three chelate rings are simultaneously released by the shift that the ligand and the Co-Cl moiety undergo with respect to each other, in the distortion toward tetrahedral coordination. The shift is accompanied by smaller changes in the C-P-C angles (*i.e.*, in the environment of phosphorus outside the coordination sphere) and by minor variations in the rest of the ligand molecule, which is essentially unstrained, as already noticed. The greater facility of rearrangements about phosphorus than about the other atoms of the ligand is evidently due to the larger orbital size and to the possibility of hybridization, which is greater for the second-row atom.

A second sort of factor which may be of importance to determine the particular coordination geometry found in

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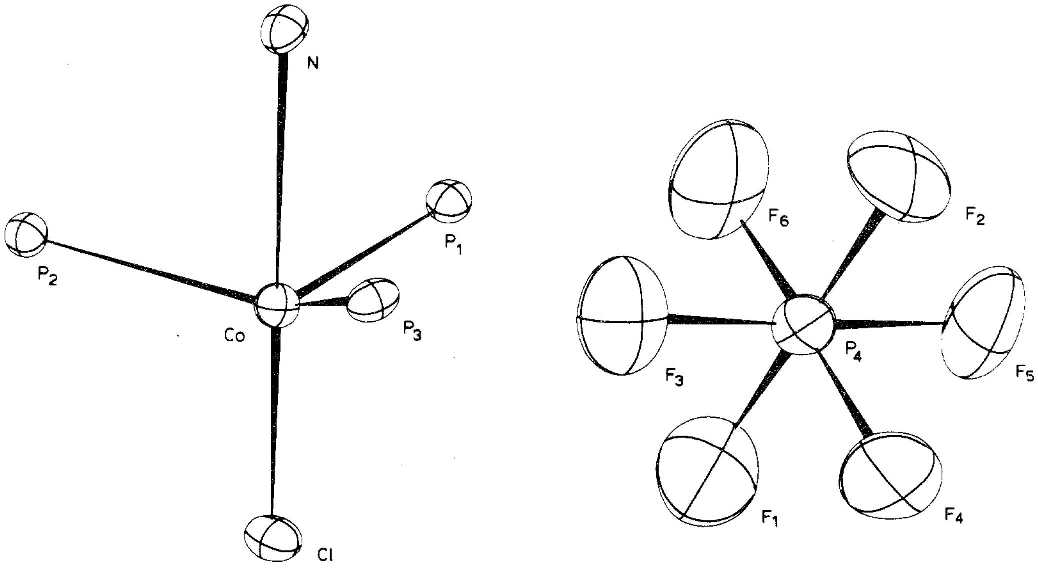

Figure 2. The 50% probability ellipsoids for the atoms refined anisotropically.

this complex is probably due to the nature of the donor set, in which the nitrogen atom differs from the others in properties like electronegativity, polarizability, and size. In this connection it should be observed that in the five-coordinate high-spin complex [Co(Me$_6$tren)Br]Br[20] [Me$_6$tren is the tripod ligand tris(2-dimethylaminoethyl)amine] having the N$_4$Br donor set, the tetrahedral distortion is quite small if appreciable at all. On the other hand, in the high-spin complex [Co(trpn)Br]Br,[21] containing a facultative tripod ligand with very long legs [trpn = tris(3-aminopropyl)amine] a sort of tetrahedral distortion opposite to the present one seems to be appearing. There the bromine atom, which differs from the average of the N$_4$Br donor set, forms an unusually long bond to the metal, which in turn moves toward a tetrahedral environment of four nitrogen atoms. It should be observed in addition that if the donor set is homogeneous, as in the five-coordinate pentakis(2-picoline *N*-oxide)cobalt(II) cation,[22] there is no tendency of high-spin Co(II) toward tetrahedral coordination. Therefore, it would seem that when the distortion from trigonal bipyramidal toward tetrahedral coordination takes place, being allowed or even favored by some tripod ligands, it tends to produce a more homogeneous environment of the metal atom. This may result in improved bonding to the metal from the atoms that remain close to it. Structural effects due to incompatibility between donor atoms have been observed and discussed in at least one case.[23]

The above considerations do not rationalize the different coordination geometry found for the high-spin cobalt complexes and the corresponding (low-spin) nickel complexes of this series. This may be unambiguously ascribed to different requirements of the two metal atoms, so that the nature of the metal atom constitutes the third and probably the most important factor to be considered here.

The high-spin state of the d^7 (Co(II)) configuration gets a larger favorable contribution from exchange than that of the d^8 (Ni(II)) configuration, due to the larger number of electrons with parallel spin, in the first case. The high-spin state, in general, should be more easily attained under a tetrahedral, rather than a five-coordinate environment, because of the lower average strength of the ligand field, in the first case. Moreover, and probably most important, as reference to the appropriate orbital diagram shows, the splitting of d orbitals in a tetrahedral ligand field (assumed here for simplicity, to represent the final stage of the distortion) again favors the d^7 with respect to the d^8 high-spin configuration. In fact, in the first case and only in that case, the energy of all singly occupied orbitals is raised and that of all doubly occupied orbitals is lowered.

Table VII. Short Contacts Involving the Fluorine Atoms[a]

F(2)···C(26^{I})	3.31	F(2)···C(21^{II})	3.28
F(2)···C(27^{I})	3.31	F(4)···C(38^{II})	3.09
F(6)···C(3^{I})	3.21	F(4)···C(39^{II})	3.30

[a] Superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z: I, $1 - x$, $1 - y$, $-z$; II, $1 - x$, $\frac{1}{2} + y$ $\frac{1}{2} - z$.

The quite different situation for low-spin cobalt complexes of this series has been discussed.[4] Electronic spectra of the high-spin cobalt complexes are consistent with an appreciable contribution of nitrogen to the ligand field, although the distortion toward tetrahedral coordination is revealed by a red shift of the bands and by an overall compression of the spectra with respect to those of true five-coordinate complexes.[1,24]

Distances and angles in the ligand molecule agree with expected values,[25] within 3σ, with the exception of the angles about phosphorus atoms. The mean C–H distance for the 33 hydrogen atoms in observed position, is 1.09 Å, slightly longer than usually found by X-ray diffraction studies. The PF$_6^-$ anion shows the usual effect of large thermal motion or partial disorder. Fluorine-phosphorus distances corrected for this effect, with the assumption of the riding model,[26] are reported in Table VI together with the uncorrected values. Figure 2 shows the thermal ellipsoids for the atoms refined anisotropically.[27] The shortest

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contacts involving fluorine atoms of the anion with other atoms in the structure are listed in Table VII. No other contact below 3.6 Å is found.

The refinement of the structures of other Co(II) complexes of this series is in progress in this laboratory.

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Structure and Magnetism of a Binuclear 1,3,5-Triketonate Complex of Cobalt(II), Bis(1,5-diphenyl-1,3-5-pentanetrionato)tetrapyridinedicobalt(II)-Tetrapyridine

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Structural and magnetic data are reported for the pyridine adduct of the binuclear cobalt(II) complex formed between 1,5-diphenyl-1,3,5-pentanetrione (H_2DBA) and $CoCl_2 \cdot 6H_2O$. Two $Co_2(DBA)_2(py)_4 \cdot 4py$, comprised of four coordinated and four uncoordinated molecules of pyridine per formula species, crystallize in a monoclinic unit cell with lattice parameters $a = 12.778$ (7), $b = 17.919$ (10), $c = 14.373$ (7) Å, and $\beta = 102.54$ (6)° and with symmetry $P2_1/n$. The structure was refined to a conventional discrepancy factor of 0.077 for 2298 independent diffractometric data for which $F^2 > 3.5\sigma(F^2)$. The molecular complex, possessing crystallographic site symmetry C_i-$\bar{1}$, consists of two cobalts coordinated to two 1,5-diphenyl-1,3,5-pentanetrionate ligands and to four pyridine ligands such that each Co(II) has an octahedral-like environment of four coplanar oxygens and two pyridine nitrogens located above and below the metal–oxygen plane. The central oxygen donor in each 1,5-diphenyl-1,3,5-pentanetrionate ligand is bonded to both cobalts thereby forming a four-membered ring containing two oxygens and two cobalts. The Co–Co distance is 3.272 (3) Å, while the intra-ring bond angles are O–Co–O = 77.28 (29)° and Co–O–Co = 102.71 (29)°. Temperature-dependent magnetic susceptibility measurements over the range 300–77°K indicate a strong antiferromagnetic interaction between the cobalts, presumably occurring *via* superexchange involving the bridging oxygens. The magnetic results are discussed in light of the structural data presented.

Introduction

The 1,3,5-triketonates represent a potentially useful class of ligands for the study of magnetic exchange between transition metals in that these ligands coordinate readily in a 1:1 molar ratio with various metals. One result of this coordination is the formation of four-membered rings containing two metal ions and two ketonic oxygens. Most work to date on chelates of 1,3,5-triketonates has dealt with the Cu(II) complexes.[1] However, complexes of Ni(II),[2] Fe(II), Mn(II), and Cr(III) have been studied in a preliminary manner,[3] and a Co(II) complex is reported herein. It is probable that the coordinating ability of the 1,3,5-triketonates will rival that of the parent 1,3-diketonates. Thus, these ligands offer an unusual opportunity to study magnetic exchange through bridging atoms in a large number of systems with similar metal environments. The work reported here was undertaken to obtain detailed stereochemical information relating to the magnetic properties of 1,3,5-triketonate metal chelates.

Experimental Section

The ligand 1,5-diphenyl-1,3,5-pentanetrione whose trivial name is dibenzoylacetone (H_2DBA) may be purchased from Eastman Organic Chemicals. It also may be conveniently prepared by the condensation of either 1-phenyl-1,3-propanedione or acetone with stoichiometric quantities of methyl benzoate in refluxing monoglyme with NaH used as the base. This procedure has been described by Miles, Harris, and Hauser.[4]

Preparation of a Powdered Sample of Bis(1,5-diphenyl-1,3-5-pentanetrionato)tetrapyridinedicobalt(II)-Dipyridine, $Co_2(DBA)_2(py)_4 \cdot 2py$. The parent compound containing coordinated water rather than coordinated pyridine molecules was prepared by the mixing of hot solutions of $CoCl_2 \cdot 6H_2O$ (1.79 g; 7.5 mmol) in 50 ml of water with H_2DBA (2.0 g; 7.5 mmol) in 150 ml of methanol. To this solution 0.3 g of NaOH in 10 ml of H_2O was added. The compound which analyzes for $Co_2(DBA)_2(H_2O)_4 \cdot 2H_2O$ precipitates immediately as a golden powder. This product was dried in a vacuum desiccator, dissolved in a minimum volume of pyridine, and filtered; the filtrate was then condensed to about half its original volume. Cooling of the solution yielded red crystals which crumble to a reddish brown powder in a vacuum desiccator. The analysis of this powder is as follows. *Anal.* Calcd for $Co_2(C_{17}H_{12}O_3)_2(C_5H_5N)_4 \cdot 2C_5H_5N$: C, 68.57; H, 4.86; N, 7.50. Found: C, 68.32; H, 5.06; N, 8.28.

Growth of Single Crystals. Single crystals were formed by dissolution of the powdered sample in hot pyridine followed by a slow cooling of the solution to room temperature over a 48-hr period. The resulting well-formed crystals decompose when exposed to X-rays in the absence of pyridine. Since the structural data reported herein establish four rather than two pyridines of crystallization per formula species, it is likely that the crystals lose pyridine and convert to the powder $Co_2(DBA)_2(py)_4 \cdot 2py$.

Single-Crystal Characterization and X-Ray Data Collection. The decomposition of the single crystals required special techniques for mounting. The crystal used for precession photographs and data collection was oriented in a glass capillary with Silastic adhesive. In order to maintain a pyridine atmosphere, the sealed capillary also contained glass wool which had been soaked in pyridine. During the entire course of data collection, pyridine could be observed in the sealed capillary. The crystal used for the X-ray study had the dimensions of 0.69 mm × 0.42 mm × 0.46 mm. The instability of the single crystals in the absence of pyridine precluded either an experimental density determination or a chemical analysis.

Precession photographs taken with Cu Kα radiation showed Laue symmetry of C_{2h}-$2/m$ with systematic absences of $h + l = 2n + 1$ for $\{h0l\}$ and $k = 2n + 1$ for $\{0k0\}$ which uniquely defined the probable space group as $P2_1/n$. The lattice constants, initially obtained from precession photographs, were refined by least squares[5] from 23 reflections whose angles were accurately determined on a

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