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Five-Coordinate Complexes. I. The Crystal and Molecular Structure of Dibromotris(diphenylphosphine)cobalt(II) and Related Compounds

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The structure of dibromotris(diphenylphosphine)cobalt(II) has been determined from three-dimensional X-ray data. The two bromide and three phosphorus atoms form a bipyramid about the cobalt with two phosphorus atoms in axial positions; the base plane of the bipyramid, made up of the third phosphorus and the two bromides, does not show trigonal symmetry. The related diphenylphosphine complexes of cobalt iodide, nickel bromide, and nickel iodide have similar structures; the unusual magnetic moment of the nickel iodide complex is explained in terms of thermal population of a low-lying triplet state.

Introduction

Complexes of cobalt(II) bromide, nickel(II) bromide, and nickel(II) iodide with diphenylphosphine (abbreviated DPP in formulas) have been reported to be five-coordinate;[1,2] Issleib and Wenschuh[1] suggested a trigonal bipyramid structure for the cobalt complex and Hayter[2] postulated a square pyramid structure for the nickel complexes.

Gillespie[3] has discussed some of the factors which affect the conformation of five-coordinate complexes of transition metals; he concludes that the trigonal bipyramid is expected when the interaction between the electron pairs is relatively more important than their interaction with the nonbonding d electrons (complexes with a large amount of "covalent" character), a square pyramid is expected when the interaction between the bonding electron pairs and the d shell predominates (complexes with essentially "ionic" bonding), and an intermediate structure is expected when the above interactions are comparable.

For complexes with d^7, d^8, or d^9 configurations, Gillespie predicts that, if the square pyramid arrangement is found, the axial bond will be longer than the basal; if the trigonal bipyramid arrangement is found, he predicts almost equivalent axial and equatorial bond lengths.

Although there seems to be support for these predictions in the copper(II) structures which have been determined, little can be said about the agreement with predictions for nickel(II) or cobalt(II) complexes because of limited structural information.

For nickel(II), the structure of dibromo(triarsine)nickel(II) has been reported;[4] the square pyramid is considerably distorted (the basal bromide is depressed *ca.* 20° below the plane), but the axial bond is elongated as predicted. Because of the distortion, the complex may be thought of as a distorted trigonal bipyramid with the angles in the base plane distorted from equivalent 120° angles to angles of approximately 90, 110, and 160°; the structure is actually intermediate to the two limiting conformations.

For cobalt(II), the structure of bis(dimethyldithiocarbamato)nitrosylcobalt(II) has been reported;[5] the compound is diamagnetic and its formulation as cobalt(II) has been questioned.[6]

The structure of the complex of nickel(II) with N-β-diethylaminoethyl-5-chlorosalicylaldimine has been described as a distorted square pyramid;[7] the structure of the complex of cobalt(II) chloride with N-methylated diethylenetriamine is distorted to such an extent that it cannot readily be described as either a square pyramid or a trigonal bipyramid.[8] For both cases, the complexes of cobalt(II) and nickel(II) have been reported to be isomorphous.

Since additional structural information is desirable for cobalt(II) and nickel(II) complexes which are five-coordinate and since the diphenylphosphine complexes offer examples of such complexes with monodentate ligands, we have investigated the structures of this series of compounds.

In addition to the general question of conformation of five-coordinate complexes, the nickel(II) diphenylphosphine complexes are interesting because of their magnetic properties; the bromide is essentially diamagnetic, but the iodide has a magnetic moment of 1.48 BM.[2] Since this value is considerably below the spin-only value for *one* unpaired electron and a spin-free nickel(II) should have two unpaired electrons, a comparison of the structures of the bromide and iodide complexes is needed to suggest a plausible explanation.

The magnetic properties of the corresponding cobalt complexes would also be of interest; only the bromide has been reported and the value of 2.01 BM[1] indicates one unpaired electron as expected for a low-spin cobalt(II).

Another observation which caused increased interest in the structure of these compounds was the observation of extreme dichroism ($Co(DPP)_3Br_2$ crystals change from red to blue when rotated 90° in polarized light) for all of the crystals. The dichroism suggested

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[1] K. Issleib and E. Wenschuh, *Z. Anorg. Allgem. Chem.*, **305**, 15 (1960).
[2] R. G. Hayter, *Inorg. Chem.*, **2**, 932 (1963).
[3] R. J. Gillespie, *J. Chem. Soc.*, 4679 (1963).
[4] G. A. Mair, H. M. Powell, and D. E. Henn, *Proc. Chem. Soc.*, 415 (1961).
[5] P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 668 (1962).
[6] A. Earnshaw, P. C. Hewlett, and L. F. Larkworthy, *Nature*, **199**, 483 (1963).
[7] L. Sacconi, P. L. Orioli, and M. DiVaira, *J. Am. Chem. Soc.*, **87**, 2059 (1965).
[8] M. DiVaira and P. L. Orioli, *Chem. Commun.*, 590 (1965).

that spectral bands in the visible region would show dramatic polarizations; this suggestion has been verified and the spectra will be the subject of a future paper.

Experimental Section

Preparation of the Complexes.—The method used by Hayter[2] for the preparation of the nickel complexes was employed to prepare the bromide and iodide complexes of both nickel and cobalt. Analytical data are summarized in Table I; all of the compounds except the cobalt iodide complex have been reported previously.

Magnetic Measurements.—Magnetic susceptibilities were determined by the Gouy method; Pascal's constants were used to calculate diamagnetic corrections. The results are summarized in Table II.

Collection and Reduction of the X-Ray Data.—X-Ray powder patterns were obtained for the four compounds using Cu Kα radiation with a Phillips diffractometer. The two bromides gave identical patterns as did the two iodides; there were slight differences both in intensities and in the *d* spacings between the bromides and iodides.

Unit cell determinations for the four compounds, using a precession camera, showed almost identical triclinic unit cells; these results are summarized in Table III.

TABLE I

ANALYTICAL DATA FOR $M(DPP)_3X_2$

M	X	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found
Co	Br	55.62	55.85	4.28	4.39
Co	I	49.62	49.83	3.82	4.02
Ni	Br	55.64	53.25	4.28	4.05
Ni	I	49.64	49.80	3.82	3.94

TABLE II

MAGNETIC DATA FOR $M(DPP)_3X_2$

M	X	$10^6\chi_g$	$10^6\chi_M$ (uncor)	Diamag cor	μ_{eff}
Co	Br	2.85	2219	248	2.43
Co	I	2.06	1997	280	2.23
Ni	Br	Dia			
Ni	I	0.47	412	280	1.29

TABLE III

UNIT CELL PARAMETERS[a] FOR $M(DPP)_3X_2$ COMPOUNDS

M	X	*a*	*b*	*c*	α	β	γ	d_{obsd}	d_{calcd}
Co	Br	11.05	11.47	15.41	98.0	82.9	118.5	1.51	1.52
Co	I	11.16	11.93	15.53	100.8	81.7	118.3	1.62	1.62
Ni	Br	11.05	11.47	15.41	98.0	82.9	118.5	1.51	1.52
Ni	I	11.16	11.93	15.53	100.8	81.7	118.3	1.62	1.62

[a] All cell dimensions were obtained from measurements of precession photographs; the interaxial angles are accurate to about 5 min and the cell edges are accurate to about 0.2%.

For the $Co(DPP)_3Br_2$ crystal, data for *hkx* and *xkl* ($x = 0$–3) zones were collected with a precession camera, Mo Kα radiation being used; from a series of timed exposures, 1566 unique reflections were estimated visually; Lorentz-polarization corrections were determined from templates.[9] No absorption corrections were made.

For the $Ni(DPP)_3I_2$ crystal, data for *hk*0 and 0*kl* zones were collected and treated in the same manner as described for the $Co(DPP)_3Br_2$ crystal; a total of 371 unique reflections were obtained.

Solution of the Structure of $Co(DPP)_3Br_2$

Application of statistical tests[10] to the principal zones of data indicated a centric structure and space group $P\bar{1}$ was assumed; the refinement of the structure confirms this choice of space group.

TABLE IV

STRUCTURE PARAMETERS FOR $Co(DPP)_3Br_2$

Atom	*x*	*y*	*z*	*B*, A^2
Co	0.3606 (4)[a]	0.0541 (3)	0.2248 (3)	1.98 (7)
Br_1	0.3151 (4)	0.1774 (3)	0.1184 (2)	3.89 (8)
Br_2	0.1943 (3)	0.9032 (3)	0.3181 (2)	3.33 (7)
P_1	0.3185 (8)	0.8921 (6)	0.1163 (5)	2.2 (1)
P_2	0.3974 (8)	0.2210 (6)	0.3259 (5)	2.6 (1)
P_3	0.5811 (8)	0.1306 (6)	0.1929 (5)	2.5 (1)
R_1C_1[b]	0.152 (4)	0.811 (3)	0.064 (3)	3.4 (6)
R_1C_2	0.057 (4)	0.859 (3)	0.081 (3)	4.4 (7)
R_1C_3	0.936 (5)	0.802 (4)	0.030 (3)	5.0 (8)
R_1C_4	0.906 (4)	0.692 (4)	0.967 (3)	4.2 (7)
R_1C_5	0.994 (4)	0.642 (4)	0.954 (3)	4.6 (7)
R_1C_6	0.111 (4)	0.693 (3)	0.006 (2)	2.9 (5)
R_2C_1	0.351 (3)	0.754 (3)	0.133 (2)	2.4 (5)
R_2C_2	0.282 (4)	0.668 (3)	0.192 (3)	3.6 (6)
R_2C_3	0.320 (5)	0.566 (4)	0.205 (3)	4.6 (7)
R_2C_4	0.423 (6)	0.567 (5)	0.154 (4)	6.8 (10)
R_2C_5	0.501 (5)	0.653 (4)	0.096 (3)	5.4 (8)
R_2C_6	0.469 (4)	0.760 (4)	0.091 (3)	4.3 (7)
R_3C_1	0.512 (3)	0.258 (3)	0.420 (2)	2.2 (5)
R_3C_2	0.535 (5)	0.171 (5)	0.447 (4)	6.3 (9)
R_3C_3	0.630 (5)	0.193 (4)	0.508 (3)	5.6 (9)
R_3C_4	0.699 (5)	0.326 (4)	0.550 (3)	5.4 (8)
R_3C_5	0.667 (5)	0.416 (5)	0.531 (3)	6.3 (10)
R_3C_6	0.575 (5)	0.392 (4)	0.460 (3)	4.8 (8)
R_4C_1	0.247 (4)	0.220 (3)	0.378 (3)	3.0 (8)
R_4C_2	0.201 (5)	0.187 (4)	0.463 (3)	5.5 (8)
R_4C_3	0.078 (6)	0.178 (5)	0.504 (4)	7.7 (12)
R_4C_4	0.015 (5)	0.215 (4)	0.453 (3)	5.2 (8)
R_4C_5	0.043 (5)	0.256 (5)	0.363 (3)	5.7 (9)
R_4C_6	0.180 (5)	0.258 (4)	0.324 (3)	5.5 (8)
R_5C_1	0.670 (3)	0.047 (3)	0.220 (2)	3.8 (7)
R_5C_2	0.601 (4)	0.947 (3)	0.288 (3)	4.1 (7)
R_5C_3	0.678 (7)	0.884 (6)	0.296 (5)	9.7 (15)
R_5C_4	0.802 (6)	0.904 (5)	0.283 (4)	8.0 (12)
R_5C_5	0.864 (5)	0.992 (5)	0.221 (3)	7.5 (11)
R_5C_6	0.802 (5)	0.070 (4)	0.183 (3)	5.7 (10)
R_6C_1	0.700 (4)	0.309 (3)	0.219 (2)	2.7 (5)
R_6C_2	0.681 (5)	0.392 (4)	0.165 (3)	4.9 (8)
R_6C_3	0.782 (5)	0.531 (4)	0.191 (3)	5.5 (9)
R_6C_4	0.868 (5)	0.571 (4)	0.254 (3)	5.1 (8)
R_6C_5	0.878 (5)	0.480 (4)	0.314 (3)	5.1 (8)
R_6C_6	0.792 (5)	0.344 (4)	0.285 (3)	4.5 (7)

[a] Numbers in parentheses here and in succeeding tables are standard deviations in the least significant digits. [b] R_1C_1 is carbon 1 of ring 1, etc.

A three-dimensional Patterson[11] synthesis revealed the bromine atom positions; cobalt and phosphorus atoms were located from a minimum function based on bromine atom vectors; carbon atoms were located in a difference Fourier synthesis phased on cobalt, bromine, and phosphorus atoms ($R = 0.24$). Full-matrix least-squares refinement, using individual isotropic temperature factors for each atom, omitting hydrogen atoms, and using all reflections weighted at unity, was continued until no parameter showed any significant change between successive cycles; the final *R* value is 0.12. Table IV lists the final structure parameters for

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(9) J. Waser, *Rev. Sci. Instr.*, **22**, 567 (1951); H. J. Grenville-Wells and S. C. Abrahams, *ibid.*, **23**, 328 (1952).

(10) E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Cryst.*, **3**, 210 (1950).

(11) All computations were made on the Burroughs B-5500 computer. Programs for Fourier summations and minimum functions were written by J. A. B.; translations of the Busing, Martin, and Levy ORFLS least-squares refinement and ORFEE function and error programs were used.

TABLE V

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $Co(DPP)_3Br_2$

H	K	L	FO	FC
2	0	0	374	492
3	0	0	300	309
4	0	0	283	266
5	0	0	71	66
6	0	0	247	279
7	0	0	118	114
8	0	0	155	192
10	0	0	138	119
2	1	0	237	248
3	1	0	63	68
4	1	0	438	431
5	1	0	202	223
6	1	0	114	113
7	1	0	63	77
8	1	0	130	124
0	2	0	329	312
1	2	0	245	162
2	2	0	276	256
4	2	0	473	485
5	2	0	182	219
6	2	0	122	123
8	2	0	71	44
0	3	0	402	369
1	3	0	435	407
2	3	0	184	185
3	3	0	152	142
4	3	0	114	112
5	3	0	84	84
8	3	0	167	178
9	3	0	170	198
11	3	0	84	88
0	4	0	307	246
1	4	0	326	312
2	4	0	346	285
3	4	0	184	220
6	4	0	95	113
8	4	0	170	164
9	4	0	138	169
0	5	0	77	54
1	5	0	195	199
2	5	0	205	211
5	5	0	63	62
6	5	0	134	124
7	5	0	100	130
0	6	0	118	112
1	6	0	241	255
2	6	0	235	222
5	6	0	71	87
6	6	0	100	95
0	7	0	176	168
1	7	0	255	253
2	7	0	184	194
6	7	0	95	77
0	8	0	130	126
1	8	0	134	127
5	8	0	134	105
6	8	0	63	57
2	9	0	95	79
4	9	0	71	78
5	9	0	63	60
1	10	0	95	142
2	10	0	134	142
4	10	0	63	87
1	11	0	134	128
4	11	0	55	68
1	12	0	89	85
-2	1	0	219	287
-3	1	0	158	182
-4	1	0	63	93
-5	1	0	164	167
-6	1	0	249	229
-7	1	0	230	237
-8	1	0	89	93
-10	1	0	71	31
-1	2	0	200	220
-2	2	0	707	707
-3	2	0	122	125
-4	2	0	261	287
-7	2	0	176	166
-9	2	0	158	148
-10	2	0	95	77
-11	2	0	100	76
-13	2	0	95	66
-1	3	0	374	359
-4	3	0	134	171
-5	3	0	148	126
-7	3	0	245	256
-8	3	0	118	139
-9	3	0	253	277
-10	3	0	190	175
-11	3	0	71	84
-13	3	0	100	103
-1	4	0	324	312
-3	4	0	365	368
-4	4	0	182	188
-5	4	0	152	120
-7	4	0	245	249
-8	4	0	263	250
-9	4	0	197	202
-10	4	0	247	211
-11	4	0	71	66
-2	5	0	100	72
-3	5	0	410	479
-4	5	0	241	213
-5	5	0	161	151
-6	5	0	212	178
-7	5	0	77	68
-8	5	0	187	184
-9	5	0	63	71
-10	5	0	130	141
-11	5	0	95	101
-1	6	0	400	380
-2	6	0	257	198
-3	6	0	272	281
-4	6	0	105	108
-5	6	0	341	414
-7	6	0	200	209
-11	6	0	71	54
-1	7	0	428	352
-2	7	0	118	94
-4	7	0	114	77
-5	7	0	315	342
-7	7	0	329	389
-8	7	0	277	236
-9	7	0	89	106
-11	7	0	71	69
-1	8	0	202	207
-2	8	0	176	182
-3	8	0	290	317
-4	8	0	173	133
-6	8	0	89	66
-7	8	0	249	260
-8	8	0	89	125
-9	8	0	95	114
-12	8	0	141	114
-1	9	0	95	83
-2	9	0	95	76
-3	9	0	224	243
-5	9	0	89	73
-7	9	0	89	108
-12	9	0	100	73
-3	10	0	71	72
-4	10	0	134	94
-6	10	0	130	92
-8	10	0	134	139
-9	10	0	138	111
-3	11	0	95	91
-4	11	0	95	78
-6	11	0	167	135
-8	11	0	170	143
-9	11	0	71	72
-4	12	0	167	132
-10	12	0	100	101
-5	13	0	95	82
-6	13	0	167	166
-8	13	0	95	84
-9	13	0	95	75
-10	13	0	95	89
-5	14	0	130	111
-6	14	0	161	148
-8	14	0	130	142
-9	14	0	95	69
2	0	1	447	283
3	0	1	557	405
4	0	1	293	254
6	0	1	141	103
7	0	1	122	108
11	0	1	77	90
1	1	1	424	321
3	1	1	155	150
4	1	1	141	119
5	1	1	134	122
7	1	1	182	201
8	1	1	138	100
1	2	1	537	446
3	2	1	158	160
4	2	1	190	192
5	2	1	327	304
6	2	1	63	72
7	2	1	164	149
10	2	1	105	110
1	3	1	367	364
2	3	1	179	158
3	3	1	435	462
4	3	1	355	334
5	3	1	155	135
6	3	1	134	155
7	3	1	100	94
9	3	1	105	123
10	3	1	110	150
1	4	1	170	153
2	4	1	114	111
3	4	1	385	387
4	4	1	243	262
6	4	1	141	120
7	4	1	179	175
8	4	1	148	150
1	5	1	187	149
3	5	1	224	204
7	5	1	148	152
8	5	1	148	152
1	6	1	202	179
2	6	1	230	221
3	6	1	138	120
4	6	1	173	117
1	7	1	71	72
2	7	1	221	193
4	7	1	179	146
2	8	1	145	106
3	9	1	105	79
2	10	1	152	153
3	10	1	105	103
2	11	1	105	110
2	-1	1	212	222
3	-1	1	625	535
4	-1	1	148	132
6	-1	1	202	229
7	-1	1	118	100
11	-1	1	148	127
3	-2	1	251	243
6	-2	1	285	253
7	-2	1	114	104
8	-2	1	232	247
1	-3	1	285	285
2	-3	1	581	516
8	-3	1	385	353
10	-3	1	138	165
11	-3	1	205	223
2	-4	1	616	500
3	-4	1	276	283
7	-4	1	55	129
8	-4	1	148	131
10	-4	1	237	278
11	-4	1	205	228
2	-5	1	274	250
4	-5	1	170	212
7	-5	1	161	131
10	-5	1	167	165
1	-6	1	141	155
2	-6	1	355	371
3	-6	1	346	309
4	-6	1	134	145
1	-7	1	217	237
2	-7	1	509	600
3	-7	1	207	213
5	-7	1	145	89
6	-7	1	167	182
8	-7	1	155	166
10	-7	1	100	122
1	-8	1	134	104
2	-8	1	415	432
4	-8	1	200	220
8	-8	1	161	154
3	-9	1	134	110
9	-9	1	141	178
1	-10	1	145	125
10	-10	1	148	72
11	-10	1	77	123
1	-11	1	105	104
3	-11	1	148	148
9	-11	1	179	177
11	-11	1	77	130
5	-12	1	105	118
1	-13	1	105	107
5	-13	1	105	134
7	-13	1	105	113
7	-14	1	105	129
9	-14	1	105	126
-2	1	1	230	226
-3	1	1	251	264
-4	1	1	134	128
-5	1	1	401	410
-6	1	1	187	215
-7	1	1	167	191
-8	1	1	219	248
-10	1	1	100	93
-1	2	1	114	129
-2	2	1	265	237
-3	2	1	570	512
-4	2	1	261	227
-5	2	1	148	169
-6	2	1	126	136
-8	2	1	173	181
-12	2	1	77	68
-1	3	1	200	172
-2	3	1	95	101
-3	3	1	279	298
-4	3	1	173	143
-5	3	1	297	309
-6	3	1	145	169
-7	3	1	192	237
-9	3	1	89	102
-12	3	1	77	105
-1	4	1	134	105
-2	4	1	286	241
-4	4	1	184	173
-6	4	1	134	158
-7	4	1	176	197
-8	4	1	64	96
-9	4	1	89	108
-5	4	1	184	210
-1	5	1	77	54
-2	5	1	329	281
-4	5	1	226	218
-8	5	1	164	179
-9	5	1	63	102
-10	5	1	138	138
-11	5	1	145	133
-3	6	1	224	168
-4	6	1	463	487
-6	6	1	363	403
-7	6	1	265	242
-9	6	1	130	65
-10	6	1	167	170
-11	6	1	145	134
-2	7	1	152	130
-3	7	1	243	209
-4	7	1	377	349
-5	7	1	145	107
-6	7	1	506	521
-7	7	1	339	330
-9	7	1	164	140
-10	7	1	138	109
-1	8	1	71	62
-2	8	1	230	238
-3	8	1	89	68
-5	8	1	155	126
-6	8	1	272	284
-7	8	1	89	119
-8	8	1	187	213
-9	8	1	71	60
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-2	9	1	197	208
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2	-5	-4	341	355
2	-5	-5	55	86
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3	0	9	77	145
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3	1	8	523	511
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3	3	4	167	201
3	3	5	176	192
3	3	7	176	211
3	3	8	130	179
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3	5	5	141	146
3	6	4	148	153
3	6	5	239	221
3	6	7	155	164
3	7	5	161	173
3	7	7	232	253
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3	-1	6	161	239
3	0	-7	145	137
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3	0	-9	245	252
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3	2	-5	276	261
3	2	-8	110	117
3	2	-9	167	106
3	2	-10	176	163
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3	2	-12	217	123
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3	4	-8	290	255
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3	5	-5	184	133
3	5	-6	212	207
3	5	-7	307	241
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3	5	-10	141	75
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3	-3	-5	152	143
3	-3	-6	122	98
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3	-3	-8	105	128
3	-3	-10	122	110
3	-3	-12	214	213
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3	-7	-4	200	216
3	-7	-7	197	205
3	-7	-9	148	140
3	-8	-4	221	219
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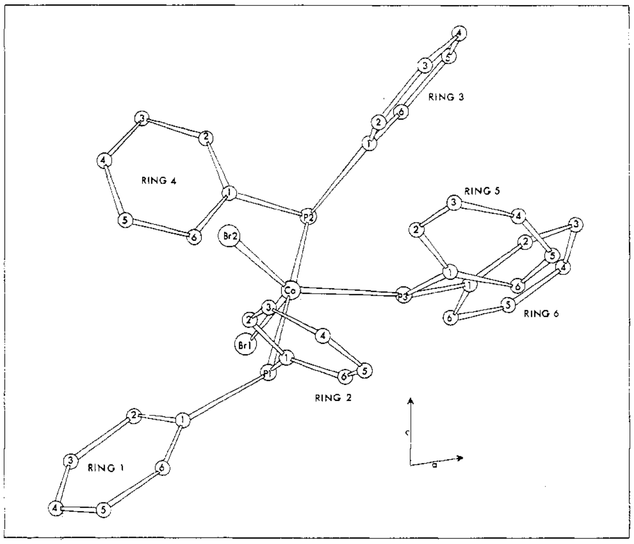

Figure 1.—A perspective drawing of one molecule of $Co(DDP)_3Br_2$ as viewed down the *b* axis of the crystal.

all atoms of the asymmetric unit except the hydrogen atoms, which were not located. The calculated structure factors (FC) obtained using these parameters are compared with the observed values (FO) in Table V.

Refinement of the Heavy-Atom Coordinates of $Ni(DPP)_3I_2$

The parameters from Table IV, substituting nickel for cobalt and iodine for bromine, were used with the data from the $Ni(DPP)_3I_2$ crystal. Since the amount of data was limited, only the parameters for nickel, iodine, and phosphorus atoms were refined by least-squares refinement; a final *R* value of 0.16 was obtained.[12] Final parameters for the atoms varied are listed in Table VI; final calculated structure factors are compared with the observed values in Table VII.

Table VI

Structure Parameters for $Ni(DPP)_3I_2$

Atom	*x*	*y*	*z*	*B*, A²
Ni	0.359 (2)	0.043 (1)	0.224 (1)	2.6 (3)
I_1	0.289 (1)	0.152 (1)	0.106 (1)	5.2 (3)
I_2	0.187 (1)	0.896 (1)	0.324 (1)	4.0 (2)
P_1	0.311 (4)	0.879 (2)	0.122 (2)	2.8 (6)
P_2	0.394 (4)	0.218 (2)	0.319 (2)	2.4 (5)
P_3	0.573 (4)	0.111 (3)	0.198 (2)	3.4 (7)

Table VII

Observed and Calculated Structure Factors for $Ni(DPP)_3I_2$

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	0	0	195	217	-7	3	0	95	127	0	2	11	87	98	0	2	-4	110	120
3	0	0	39	52	-8	3	0	26	32	0	2	12	70	69	0	2	-5	157	165
4	0	0	40	28	-9	3	0	109	120	0	2	13	30	36	0	2	-6	45	42
6	0	0	77	70	-10	3	0	42	40	0	3	1	69	85	0	2	-7	201	198
8	0	0	63	58	-1	4	0	102	112	0	3	2	292	285	0	2	-8	84	110
9	0	0	42	30	-2	4	0	73	69	0	3	4	335	315	0	2	-10	44	46
10	0	0	32	38	-3	4	0	123	126	0	3	5	111	100	0	2	-11	26	35
11	0	0	32	22	-4	4	0	77	66	0	3	6	104	109	0	2	-12	55	65
2	1	0	118	106	-7	4	0	95	93	0	3	7	109	85	0	2	-14	42	46
3	1	0	44	33	-8	4	0	58	61	0	3	9	65	75	0	2	-16	45	50
4	1	0	137	125	-9	4	0	62	88	0	3	11	28	43	0	3	-1	118	136
6	1	0	81	53	-10	4	0	41	39	0	3	12	51	42	0	3	-2	162	168
7	1	0	62	43	-11	4	0	44	46	0	3	13	73	79	0	3	-3	37	6
8	1	0	71	65	-13	4	0	22	4	0	3	14	32	38	0	3	-4	28	9
9	1	0	42	39	-1	5	0	46	37	0	3	15	100	47	0	3	-5	340	324
10	1	0	32	16	-2	5	0	83	85	0	4	1	44	45	0	3	-6	107	80
11	1	0	22	16	-3	5	0	175	181	0	4	2	70	70	0	3	-7	141	125
0	2	0	76	67	-4	5	0	98	91	0	4	3	102	112	0	3	-9	55	40
1	2	0	87	74	-5	5	0	88	84	0	4	4	262	210	0	3	-10	141	111
2	2	0	123	114	-6	5	0	47	61	0	4	5	48	48	0	3	-14	67	87
3	2	0	42	23	-8	5	0	53	55	0	4	6	167	171	0	3	-15	30	35
4	2	0	174	206	-9	5	0	48	25	0	4	9	87	89	0	3	-16	45	64
5	2	0	26	15	-10	5	0	30	30	0	4	12	22	20	0	4	-1	77	90
6	2	0	89	80	-11	5	0	30	37	0	4	13	75	83	0	4	-2	67	85
7	2	0	40	23	-13	5	0	45	21	0	4	14	44	42	0	4	-3	127	111
9	2	0	32	5	-1	6	0	79	84	0	4	15	45	58	0	4	-5	180	261
0	3	0	132	152	-2	6	0	69	40	0	5	2	212	189	0	4	-6	115	138
1	3	0	101	87	-3	6	0	120	141	0	5	3	17	3	0	4	-7	41	33
2	3	0	155	143	-5	6	0	142	173	0	5	4	72	70	0	4	-8	42	48
4	3	0	139	121	-6	6	0	35	36	0	5	6	146	136	0	4	-9	51	35
5	3	0	26	21	-7	6	0	68	77	0	5	7	48	52	0	4	-10	65	65
6	3	0	49	40	-1	7	0	93	106	0	5	8	56	56	0	4	-12	40	35
8	3	0	61	51	-2	7	0	83	69	0	5	9	50	48	0	4	-14	68	64
9	3	0	32	26	-3	7	0	45	37	0	5	10	66	61	0	4	-15	30	33
10	3	0	22	12	-5	7	0	128	141	0	5	11	42	48	0	5	-3	205	188
0	4	0	136	151	-7	7	0	118	121	0	5	12	44	41	0	5	-4	17	9
1	4	0	102	87	-8	7	0	39	52	0	5	13	32	32	0	5	-5	35	43
2	4	0	152	155	-9	7	0	50	45	0	5	15	32	32	0	5	-7	26	45
3	4	0	63	51	-12	7	0	22	21	0	5	16	22	17	0	5	-8	37	42
4	4	0	81	59	-1	8	0	94	95	0	6	2	132	156	0	5	-9	39	59
6	4	0	51	36	-3	8	0	82	75	0	6	4	26	22	0	5	-10	20	10
7	4	0	22	24	-4	8	0	47	32	0	6	6	69	72	0	5	-12	77	87
8	4	0	93	81	-5	8	0	26	20	0	6	7	40	53	0	5	-14	22	36
9	4	0	32	24	-7	8	0	79	73	0	6	8	77	84	0	6	-1	172	193
10	4	0	30	23	-9	8	0	41	41	0	6	10	42	38	0	6	-3	172	141
0	5	0	93	65	-12	8	0	44	50	0	6	11	62	53	0	6	-5	37	44
1	5	0	50	39	-1	9	0	59	63	0	6	12	32	32	0	6	-6	70	93
2	5	0	78	63	-3	9	0	87	89	0	6	15	22	10	0	6	-7	66	61
6	5	0	86	67	-5	9	0	49	45	0	7	1	39	32	0	6	-8	26	21
8	5	0	69	45	-3	10	0	52	49	0	7	2	28	42	0	6	-10	86	99
1	6	0	93	61	-5	10	0	51	48	0	7	3	40	41	0	6	-11	30	27
3	6	0	28	10	-6	10	0	30	19	0	7	4	114	113	0	6	-12	79	96
4	6	0	88	52	-7	10	0	30	36	0	7	8	85	99	0	6	-13	22	13
6	6	0	69	51	-8	10	0	42	47	0	7	10	53	53	0	7	-1	162	166
8	6	0	30	12	-3	11	0	30	42	0	7	12	22	25	0	7	-2	28	28
1	7	0	110	92	-5	11	0	30	35	0	7	13	32	34	0	7	-3	55	73
3	7	0	30	19	-6	11	0	42	37	0	8	1	71	74	0	7	-5	56	58
4	7	0	61	40	-7	11	0	30	35	0	8	2	30	39	0	7	-6	74	96
6	7	0	22	18	-8	11	0	53	55	0	8	4	73	91	0	7	-7	20	3
0	8	0	28	23	-4	12	0	44	52	0	8	5	22	35	0	7	-8	20	14
1	8	0	84	78	-4	13	0	30	37	0	8	6	30	35	0	7	-10	88	119
4	8	0	32	21	-6	13	0	44	41	0	8	7	30	35	0	7	-11	30	37
5	8	0	30	16	-4	14	0	30	20	0	8	8	44	42	0	7	-12	42	50
0	9	0	30	32	-6	14	0	42	41	0	8	10	44	34	0	7	-14	22	4
3	9	0	30	17	-8	14	0	30	31	0	8	13	30	30	0	8	-1	104	87
5	9	0	42	29	0	0	3	52	41	0	9	1	67	70	0	8	-2	41	26
3	10	0	52	48	0	0	4	77	49	0	9	2	30	28	0	8	-3	28	46
5	10	0	39	22	0	0	5	212	188	0	9	3	53	53	0	8	-5	41	73
1	11	0	44	50	0	0	6	44	54	0	9	5	22	29	0	8	-8	66	80
3	11	0	49	41	0	0	7	62	77	0	9	6	61	55	0	8	-10	42	73
1	12	0	61	38	0	0	8	67	71	0	9	10	22	15	0	9	-3	60	59
3	12	0	24	17	0	0	9	267	224	0	10	1	30	39	0	9	-5	22	19
1	13	0	50	21	0	0	10	126	101	0	10	3	69	72	0	9	-6	60	71
-2	1	0	141	151	0	0	11	65	71	0	10	5	22	16	0	9	-8	68	79
-4	1	0	59	81	0	0	14	66	61	0	10	6	30	33	0	10	-1	44	42
-5	1	0	95	96	0	1	2	212	178	0	10	8	30	29	0	10	-3	30	29
-6	1	0	33	41	0	1	3	30	25	0	11	3	53	45	0	10	-6	69	103
-7	1	0	92	81	0	1	5	160	146	0	11	5	20	23	0	10	-8	44	49
-11	1	0	45	39	0	1	8	22	30	0	11	8	28	22	0	10	-10	22	15
-13	1	0	32	17	0	1	9	173	157	0	12	0	20	21	0	11	-1	30	36
-2	2	0	255	236	0	1	10	51	61	0	12	1	30	30	0	11	-4	44	43
-3	2	0	71	74	0	1	11	93	119	0	12	5	20	25	0	11	-6	42	54
-4	2	0	108	112	0	1	12	40	37	0	13	1	26	26	0	11	-7	22	19
-5	2	0	81	90	0	1	14	52	45	0	1	-2	150	124	0	11	-10	30	34
-6	2	0	32	39	0	1	16	32	26	0	1	-3	89	98	0	12	-1	30	39
-7	2	0	89	102	0	2	2	410	433	0	1	-4	177	133	0	12	-2	22	28
-9	2	0	70	61	0	2	3	113	101	0	1	-5	69	79	0	12	-4	42	49
-10	2	0	30	30	0	2	4	339	300	0	1	-7	167	145	0	12	-8	30	23
-11	2	0	32	26	0	2	5	28	21	0	1	-8	55	61	0	12	-10	20	31
-13	2	0	32	29	0	2	6	30	25	0	1	-9	159	140	0	13	-2	28	33
-1	3	0	87	115	0	2	7	114	96	0	1	-10	61	68	0	13	-4	20	29
-4	3	0	59	55	0	2	8	54	58	0	1	-12	55	36	0	13	-8	26	23
-6	3	0	22	34	0	2	10	26	24	0	1	-16	22	32					

Discussion

The Coordination Sphere.—Bond distances and angles for the heavy atoms of the two structures are given in Table VIII; Figure 1 is a drawing of the structure with atoms labeled. The coordination sphere, *i.e.*, the atoms bonded to the metal, forms a bipyramid. The two bromine atoms, one phosphorus atom (P_3), and the metal atom are essentially coplanar; in $Co(DPP)_3Br_2$, the dihedral angle between the plane defined by $Co–Br_1–Br_2$ and the plane defined by $Co–P_3–Br_1$ is only 1.9°. Furthermore, the angles between the equatorial groups and each axial group are approximately 90°—in $Co(DPP)_3Br_2$, the angles between equatorial groups and P_1 are 90.8, 86.8, and 89.8°; between equatorial groups and P_2, the angles are 91.1, 89.2, and 91.3°. Since the three atoms in the equatorial plane are not equivalent, trigonal symmetry in this plane is not possible and the structure is not a *trigonal* bipyramid; angles between groups in the equatorial plane range from 98 to 136° instead of the 120° required for trigonal symmetry.

The structures, as predicted by Gillespie,[3] are neither trigonal bipyramid nor square pyramid, but can be thought of as intermediate to the two. The structures can be described as distorted from a trigonal bipyramid

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[12] One of the referees carried out additional refinement, which included refining the phenyl groups as rigid bodies, and obtained an *R* value of 0.147 after six cycles. Most heavy-atom parameters were unchanged; no interatomic distance or angle was changed by more than twice the quoted standard deviation.

TABLE VIII

SELECTED INTRAMOLECULAR DISTANCES AND ANGLES FOR $M(DPP)_3X_2$

	Intramolecular distance, A			Angle, deg	
Atoms	M = Co; X = Br	M = Ni; X = I	Atoms	M = Co; X = Br	M = Ni; X = I
$M-X_1$	2.54 (1)	2.80 (2)	X_1-M-X_2	125.6 (2)	123 (1)
$M-X_2$	2.33 (1)	2.49 (2)	X_1-M-P_1	86.8 (3)	87 (1)
$M-P_1$	2.23 (1)	2.18 (3)	X_1-M-P_2	89.2 (3)	87 (1)
$M-P_2$	2.20 (1)	2.22 (3)	X_1-M-P_3	98.1 (3)	105 (1)
$M-P_3$	2.18 (1)	2.13 (5)	X_2-M-P_1	90.9 (3)	89 (1)
$P_1-R_1C_1$	1.85 (4)		X_2-M-P_2	91.1 (3)	93 (1)
$P_1-R_2C_1$	1.85 (3)		X_2-M-P_3	136.3 (3)	133 (1)
$P_2-R_3C_1$	1.91 (3)		P_1-M-P_2	175.9 (4)	174 (2)
$P_2-R_4C_1$	1.75 (4)		P_1-M-P_3	89.9 (4)	93 (2)
$P_3-R_5C_1$	1.78 (4)		P_2-M-P_3	91.3 (4)	91 (1)
$P_3-R_6C_1$	1.84 (3)				
				Dihedral angle, deg	
			X_1-M-X_2 P_3-M-X_2	1.9 (3)	

by increasing one equatorial angle to 136° and decreasing another to 98°; again as predicted, there is no significant difference in the axial and equatorial M–P distances.

The structures can also be described as distorted from a square pyramid in the same manner as Ni(triarsine)Br_2; the basal bromine atom is depressed *ca.* 46° below the plane as compared to *ca.* 20° in the triarsine complex; as in the triarsine complex, the axial M–Br distance is significantly longer than the basal M–Br distance.

Although it may be primarily a matter of taste, it seems more reasonable to think of the structure as a distorted trigonal bipyramid; in considering polarized spectra, it is certainly the preferred approach since the polarized spectra can be interpreted in terms of C_s symmetry, retaining only the horizontal symmetry plane of D_{3h} symmetry. The descent from D_{3h} to C_s can be made without change in axial designations and without change in orbital designations; the same is *not* true in going from C_{4v} to C_s symmetry.

Furthermore, in D_{3h} symmetry, the d_{xy} and $d_{x^2-y^2}$ orbitals are degenerate in energy as are the d_{xz} and d_{yz}; the primary effect of the distortion, due to both angular distortion and to the difference in groups within the equatorial plane, will be in the trigonal plane and will, thus, remove the degeneracy of the d_{xy} and $d_{x^2-y^2}$ orbitals; a smaller effect would be experienced by the d_{xz} and d_{yz} orbitals. Considering the square pyramid structure, the highest energy orbital, the $d_{x^2-y^2}$, would be lowered considerably and one of the lowest energy orbitals, the d_{xz} or d_{yz}, would be raised considerably; the ordering of the orbitals in the lower symmetry is not obvious because of the rather large distortion involved.

The bipyramid structure of $Co(DPP)_3Br_2$ violates the general rule[13] that the more electronegative ligands are always in the axial positions. There does not appear to be any steric factor which would prevent the more electronegative halogen atoms from occupying the axial positions.

One further fact concerning the coordination sphere should be mentioned; LaPlaca and Ibers[14] indicated that, in the square pyramidal dichlorotris(triphenylphosphine)ruthenium(II), the sixth corner of the octahedron was occupied by a phenyl hydrogen atom. If the $Co(DPP)_3Br_2$ structure is considered, the closest carbon atom (R_2C_2) is only 3.68 A away and, although the hydrogen atom would be farther from the metal atom than in the ruthenium compound, the sixth position of an octahedron would be effectively blocked.

Phenyl Groups.—The errors in carbon atom positions are rather large and these positions could possibly have been improved by further refinement, particularly by introducing anisotropic temperature factors for the heavy atoms and by using a different weighting of reflections in the refinement. However, our principal interest was not in the carbons and refinement was not continued. The carbon–carbon distances obtained, Table IX, range from 1.28 to 1.55 A; the average bond distance for each ring is also given in Table IX; there is little difference in the various rings and there is reasonable agreement with the expected 1.39 A.

TABLE IX

CARBON–CARBON DISTANCES OF THE PHENYL GROUPS

Atoms	Ring 1	Ring 2	Ring 3	Ring 4	Ring 5	Ring 6
C_1-C_2	1.39 (5)	1.32 (4)	1.28 (6)	1.39 (5)	1.52 (5)	1.44 (5)
C_2-C_3	1.46 (6)	1.46 (5)	1.39 (6)	1.39 (6)	1.38 (7)	1.48 (5)
C_3-C_4	1.32 (6)	1.30 (6)	1.44 (5)	1.34 (7)	1.28 (8)	1.32 (6)
C_4-C_5	1.40 (5)	1.32 (6)	1.32 (6)	1.49 (6)	1.36 (7)	1.54 (6)
C_5-C_6	1.44 (5)	1.45 (6)	1.50 (6)	1.54 (6)	1.55 (7)	1.42 (5)
C_6-C_1	1.42 (4)	1.36 (5)	1.43 (4)	1.41 (6)	1.41 (5)	1.40 (5)
Av	1.41	1.37	1.39	1.43	1.42	1.43

We were interested in the orientation of the two phenyl groups of each diphenylphosphine ligand. Although few structures are known for complexes containing phosphines with two or three phenyl groups, those that have been studied[14,15] apparently show no preferred dihedral angle between phenyl groups. The lack of such orientation is surprising since, in the phenyl-substituted phosphines, additional back-donation from the metal d orbitals to phosphorus d orbitals could be stabilized if the π system of each phenyl group were to interact with phosphorus d orbitals to further delocalize this back-donation, and, if this suggestion is correct, there should be a definite orientation of phenyl groups with respect to phosphorus d orbitals and, thus, with respect to other phenyl rings on the same phosphorus.

The absence of a definite phenyl orientation in complexes of tertiary phosphines could, of course, be due to a steric problem; the diphenylphosphine ligands of the cobalt bromide complex should be a better measure of such effects.

For the axial phosphines, the dihedral angle between the two phenyl groups (82° for P_1 and 83° for P_2) is close to 90° and may suggest that the phenyl groups are entering into d-p π bonding with different phosphorus orbitals; the third phosphine does not show such orientation—the dihedral angle is only 69°. Steric crowding

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[13] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963); E. L. Muetterties, W. Mahler, S. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964).

[14] S. J. LaPlaca and J. A. Ibers, *ibid.*, **4**, 778 (1965).

[15] R. Eisenberg and J. A. Ibers, *ibid.*, **4**, 773 (1965).

would certainly be greater in the vicinity of this phosphine and could prevent the proper orientation. It is also possible that π bonding to this phosphine is less important although the equivalence of the three Co–P distances argues against this possibility.

Magnetic Properties.—Five-coordinate complexes of nickel which contain phosphorus or arsenic ligands are usually diamagnetic; the nickel iodide complex with diphenylphosphine is the only example of a paramagnetic complex of this type. This paramagnetism could, in the absence of structural data, be attributed to either a difference in structure or to the difference in field strength for the nickel iodide and nickel bromide complexes. Since unit cell parameters and the intensity of every line in the powder patterns for the cobalt bromide and nickel bromide complexes were identical, it was valid to conclude that the structures were identical. Although the similarity of the unit cells of the nickel iodide and cobalt bromide complexes suggested related structures, there was sufficient difference in intensities of individual reflections to make such a conclusion questionable. However, the successful refinement of the heavy-atom coordinates using two zones of intensity data from the nickel iodide crystal shows that the iodide and bromide structures are essentially identical; the only differences appear related to the difference in size of the bromine and iodine atoms.

The explanation of the paramagnetism of the nickel iodide complex must be related to the ligand field strength. Since the moment of 1.29 BM is considerably below the value for one unpaired electron (although two unpaired electrons would be present in a spin-free nickel(II) complex), the complex must be near the "cross-over point" where the ground state changes from singlet to triplet. Due to the closeness of these two levels, there could be population of both levels and, therefore, an intermediate moment.

The complexes of cobalt bromide and cobalt iodide have moments (2.43 and 2.23 BM, respectively) which are consistent with the presence of one unpaired electron. Although the values are above the spin-only value of 1.73 BM, the difference is probably due to the orbital contribution.

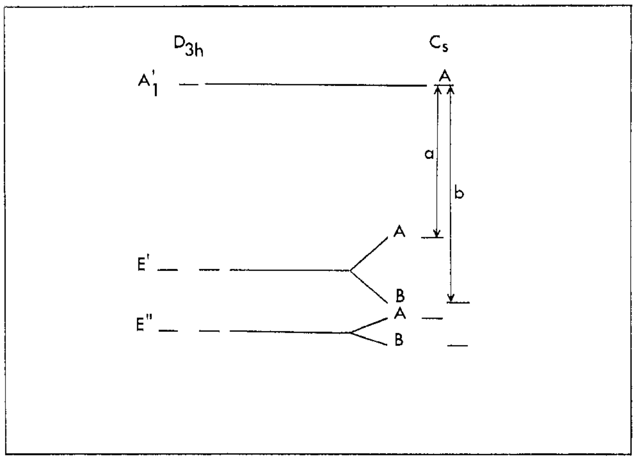

Figure 2.—The splitting of d orbitals in D_{3h} and C_s symmetries. Arrows indicate the difference in crystal field stabilization energy for high- and low-spin complexes of: (a) nickel(II) and (b) cobalt(II).

Since the two cobalt complexes are essentially low-spin, this would indicate that, assuming similar crystal field splittings for the cobalt and nickel ions, the "cross-over point" for cobalt(II) is at a lower *Dq* value than that for nickel(II). Although the change in crystal field stabilization energy in going from a high-spin to a low-spin state would be the same for d^7 or d^8 complexes in D_{3h} symmetry, the further removal of d orbital degeneracies in C_s symmetry would make the low-spin state more favorable for d^7 than for d^8. This is shown in Figure 2, where the changes in crystal field stabilization energy between the high-spin and low-spin states are indicated for d^7 and d^8 complexes; due to this larger difference between high-spin and low-spin stabilizations, d^7 complexes should become spin-paired at lower *Dq* values than d^8 complexes, as observed.

Conclusions

Although five-coordinate complexes which are largely covalent, such as $Fe(CO)_5$, are expected to show a trigonal bipyramid arrangement, and five-coordinate complexes which have large *Dq* values, such as the ruthenium complex discussed above, are expected to show a square pyramid arrangement, most five-coordinate complexes of metal ions of the first transition series are expected to be intermediate to these extremes and are, thus, expected to show conformations intermediate to the trigonal bipyramid and square pyramid arrangements. The structures of $Co(DPP)_3Br_2$ and the related $M(DPP)_3X_2$ compounds can be described as bipyramidal, but they are distorted from a trigonal bipyramid arrangement and could, thus, be described as an intermediate structure. It is interesting to note that the $Ni(triarsine)Br_2$ structure, usually described as a square pyramid, is also such an intermediate structure and is also very close to a bipyramid structure.

The phenyl groups of two of the phosphines show dihedral angles close to 90° and this may be evidence of participation of the phenyl groups in the back-donation mechanism.

The magnetic moments of the cobalt complexes and the nickel bromide complex indicate that these are normal low-spin complexes; the paramagnetism of the nickel iodide complex is probably due to thermal population of the low-lying triplet state.

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