Electronic Supporting Information

Preparation and characterization of mixed-ligand cobalt(III) complexes containing (3-aminopropyl)dimethylphosphine (pdmp). Conformation of the six-membered pdmp chelate ring

Takayoshi Suzuki,[*a] Katsuhiro Fujiwara,[b] Hideo D. Takagi[b] and Kazuo Kashiwabara[b]

[a] *Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka 560-0043, Japan. Tel: +81-6-6850-5410; Fax: +81-6-6850-5408; E-mail: suzuki@chem.sci.osaka-u.ac.jp*

[b] *Graduate School of Science, and Research Center for Materials Science, Nagoya University, Furocho, Chikusa, Nogoya 464-8602, Japan.*

(1) Crystal structures of the dichloro complexes: trans(Cl,Cl)cis(P,P)-$[CoCl_2(pdmp)_2]PF_6$

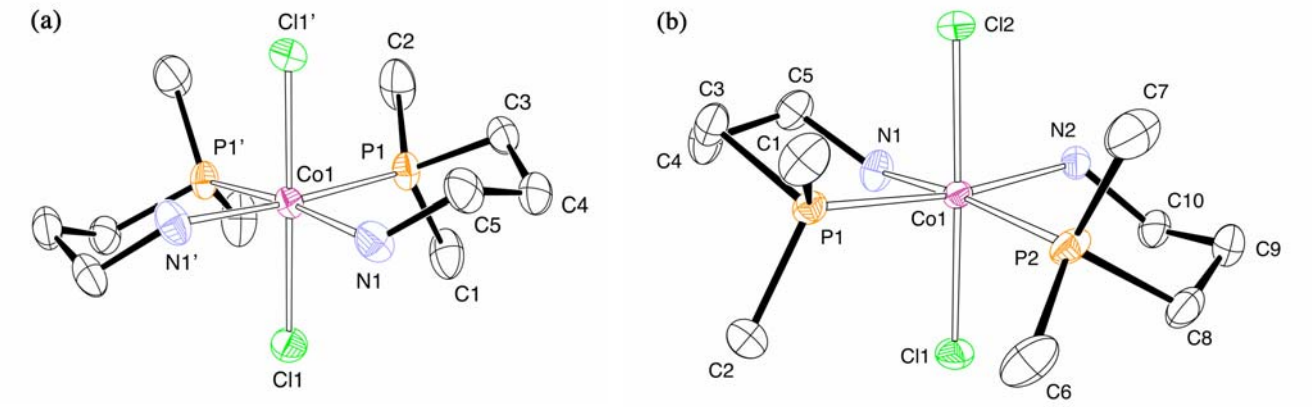
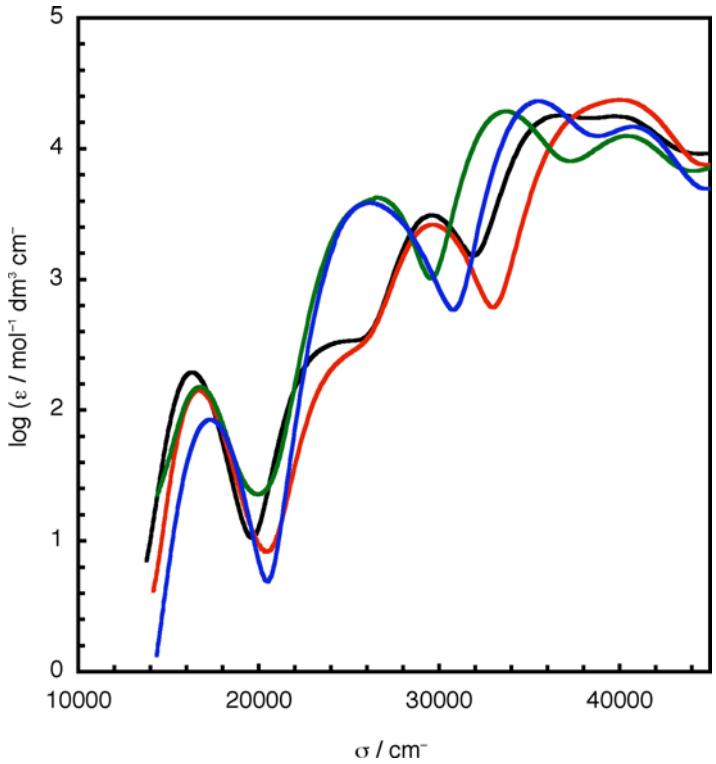


Fig. S1 Comparison of molecular structures of *trans(Cl,Cl)cis(P,P)*-$[CoCl_2(pdmp)_2]^+$ in (a) **1**•CH_3CN (30% probability level) and (b) **1** (50% probability level).

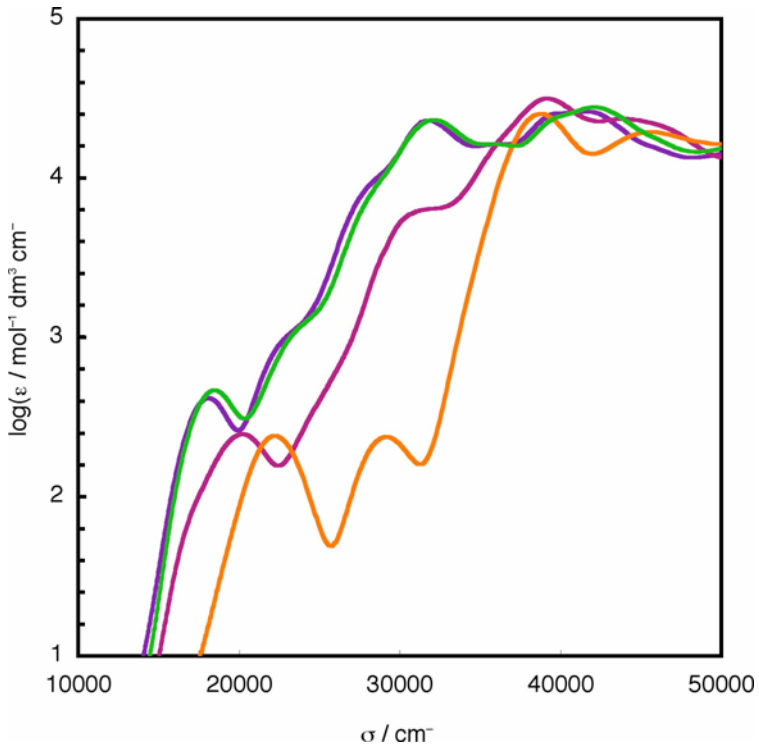
Table S1 Comparisons of geometrical parameters (Å, °) of *trans(Cl,Cl)cis(P,P)*-$[CoCl_2(pdmp)_2]^+$ in **1**•CH_3CN and **1**.

1•CH_3CN		**1**			
Co1–Cl1	2.2423(14)	Co1–Cl1	2.252(2)	Co1–Cl2	2.246(2)
Co1–P1	2.2328(14)	Co1–P1	2.225(2)	Co1–P2	2.223(2)
Co1–N1	2.070(4)	Co1–N1	2.053(3)	Co1–N2	2.049(3)
Cl1–Co1–Cl1’	176.67(8)	Cl1–Co1–Cl2	177.73(3)		
Cl1–Co1–P1	87.57(6)	Cl1–Co1–P1	93.80(10)	Cl1–Co1–P2	86.52(8)
Cl1–Co1–P1’	94.73(6)	Cl2–Co1–P1	85.71(10)	Cl2–Co1–P2	95.74(8)
Cl1–Co1–N1	90.74(13)	Cl1–Co1–N1	85.77(11)	Cl1–Co1–N2	94.05(12)
Cl1–Co1–N1’	86.84(13)	Cl2–Co1–N1	92.01(11)	Cl2–Co1–N2	86.32(12)
P1–Co1–P1’	93.14(7)	P1–Co1–P2	95.20(7)		
P1–Co1–N1	89.99(13)	P1–Co1–N1	89.58(9)	P1–Co1–N2	171.57(7)
P1–Co1–N1’	173.81(11)	P2–Co1–N1	171.18(8)	P2–Co1–N2	88.33(10)
N1–Co1–N1’	87.4(2)	N1–Co1–N2	87.95(12)		
Co1–P1–C3–C4	47.8(5)	Co1–P1–C3–C4	51.6(3)	Co1–P2–C8–C9	49.9(3)
P1–C3–C4–C5	–66.3(5)	P1–C3–C4–C5	–67.0(3)	P2–C8–C9–C10	–62.1(3)
C3–C4–C5–N1	70.9(6)	C3–C4–C5–N1	68.0(4)	C8–C9–C10–N2	67.9(3)
Co1–N1–C5–C4	–65.3(6)	Co1–N1–C5–C4	–62.8(4)	Co1–N2–C10–C9	–71.5(3)

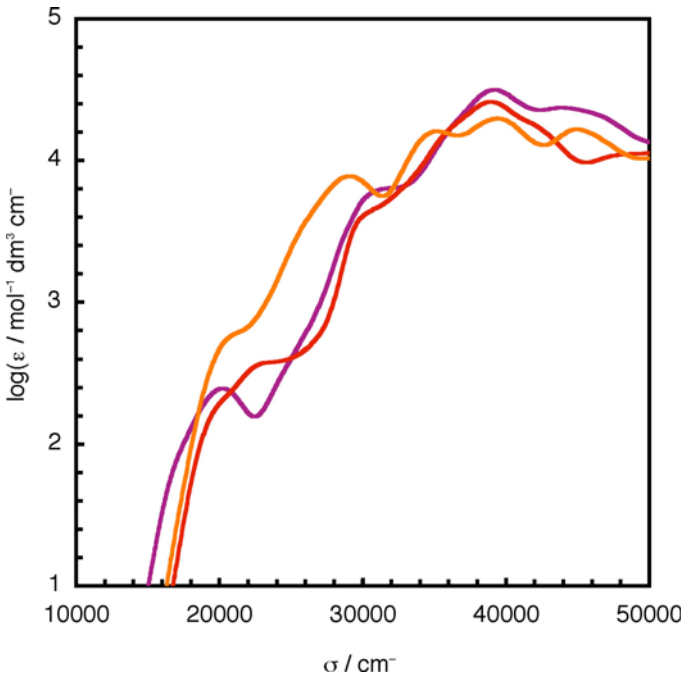
(2) UV-vis absorption spectra of the pdmp and the related complexes:



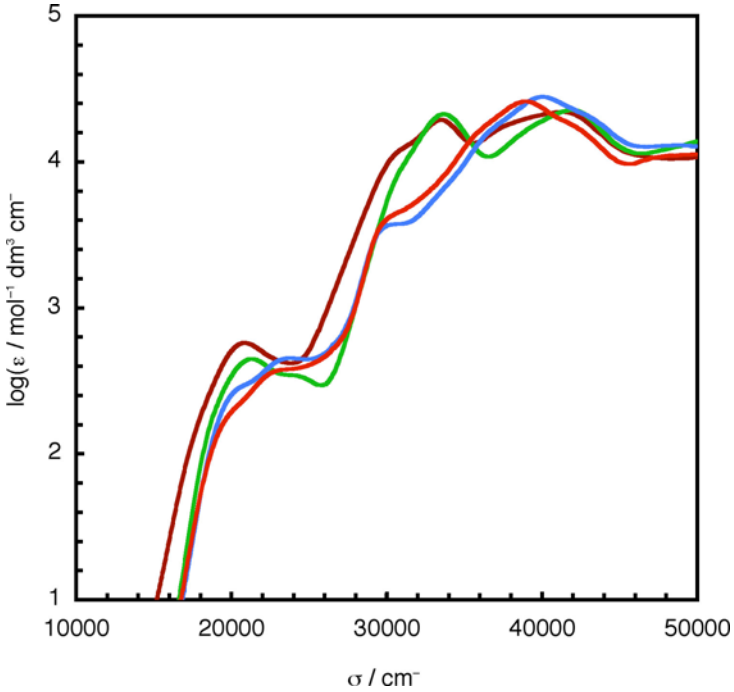
Fig, S2 (a) UV-vis absorption spectra of complexes **1** (black), **2** (red), **3** (green) and **4** (blue) in acetonitrile at ambient temperature.



Fig, S2 (b) UV-vis absorption spectra of complexes **5** (orange) in water, **6** (red-purple), **9** (blue-purple) and **11** (light green) in acetonitrile at ambient temperature.



Fig, S2 (c) UV-vis absorption spectra of complexes **6** (red-purple), **7a** (red) and **7b** (orange) in acetonitrile at ambient temperature.



Fig, S2 (d) UV-vis absorption spectra of complexes **7a** (red), **8** (aqua), **10** (reddish brown) and **12** (yellow-green) in acetonitrile at ambient temperature.

(3) DFT optimun geometry calculation

The calculations were performed using Oxford CAChe 3.2 program system. Each model conformer generated was at first refined by the MM3 calculation, and then the geometry was optimized by the DGauss DFT method. The DZVP basis sets and B88-LYP energy functional was used, and the density mixing parameter was set to be 0.1. Level shift was ignored during the calculation. The threshold of the gradient used to terminate the optimization was 0.0008 Hartree/Bohr, and the self-consistent wavefunction convergence criteria for the orbital rotation gradient and the energy were 0.0005 and 0.0000005, respectively. .

$[Co(en)_2(pdmp)]^{3+}$: The DFT optimum geometry calculation was perfored in the following four conformers, *trans(lel,chair)-lel•ob•chair*, *cis(lel,chair)-lel•ob•chair*, *lel_2•chair* and *ob_2•chair*. The relative energy difference among the conformers were: *cis(lel,chair)-lel•ob•chair*: –0.18 kJ mol^{-1} < *trans(lel,chair)-lel•ob•chair*: 0 kJ mol^{-1} < *lel_2•chair*: 0.06 kJ mol^{-1} < *ob_2•chair*: 0.48 kJ mol^{-1} (Fig. S3). In Table S2 the calculated geometrical parameters for *trans(lel,chair)-lel•ob•chair* conformer were compared to the actual structural parameters of complex **5** determined by X-ray analysis

$[CoCl_2(pdmp)_2]^+$: For the dichlorobis(pdmp) complexes, several conformers for five geometrical isomers were examined by the DFT optomum geometry calculation. The energy of the most stable structure, (C_2)-*$chair_2$-trans(Cl,Cl)cis(P,P)*- $[CoCl_2(pdmp)_2]^+$ that was consistent with the observed structure in the X-ray analysis of **1** (and **1**•CH_3CN), was set to be zero. The results are illustrated in Fig. S4 (a)–(d). In Tables S3–S6, the calculated geometrical parameters for (C_2)-*$chair_2$-trans(Cl,Cl)cis(P,P)*, *syn-$chair_2$-cis(Cl,Cl)trans(P,N)*, *trans-chair•lel-cis(Cl,Cl)-trans(P,N)* and *anti-$chair_2$-cis(Cl,Cl)trans(N,N)* conformers were compared to the X-ray derived structural parameters of complexes **1**, **7a**, **10'** and **7b**, respectively.

***trans*-$[CoCl_2(dmpp)_2]^+$:** Five conformers of *trans*-$[CoCl_2(dmpp)_2]^+$ were calculated by the DFT method, and the results are collected in Fig. S5. The relative energies, that of the most stable conformer of (D_{2d})-*$twist_2$* was set to be zero, were (C_{2i})-*$chair_2$*: 5.70 kJ mol^{-1}, *chair•twist*: 21.19 kJ mol^{-1}, (C_{2v})-*$chair_2$*: 23.63 kJ mol^{-1}, (C_{2h})-*$twist_2$*: 39.54 kJ mol^{-1}. In Table S7 the calculated geometrical parameters for (D_{2d})-*$twist_2$* conformer were compared to the X-ray derived structural parameters in complex **3**.

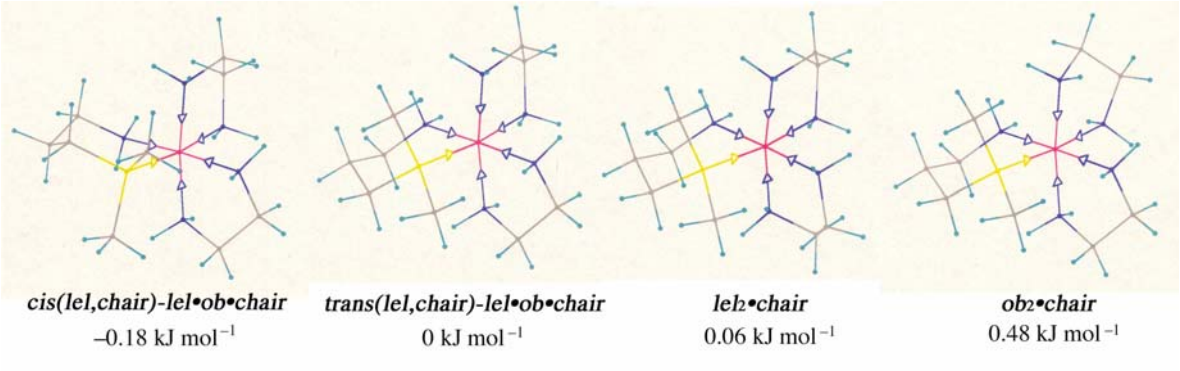


Fig. S3 The optimized structures and the relative energies of some conformers of $[Co(en)_2(pdmp)]^{3+}$.

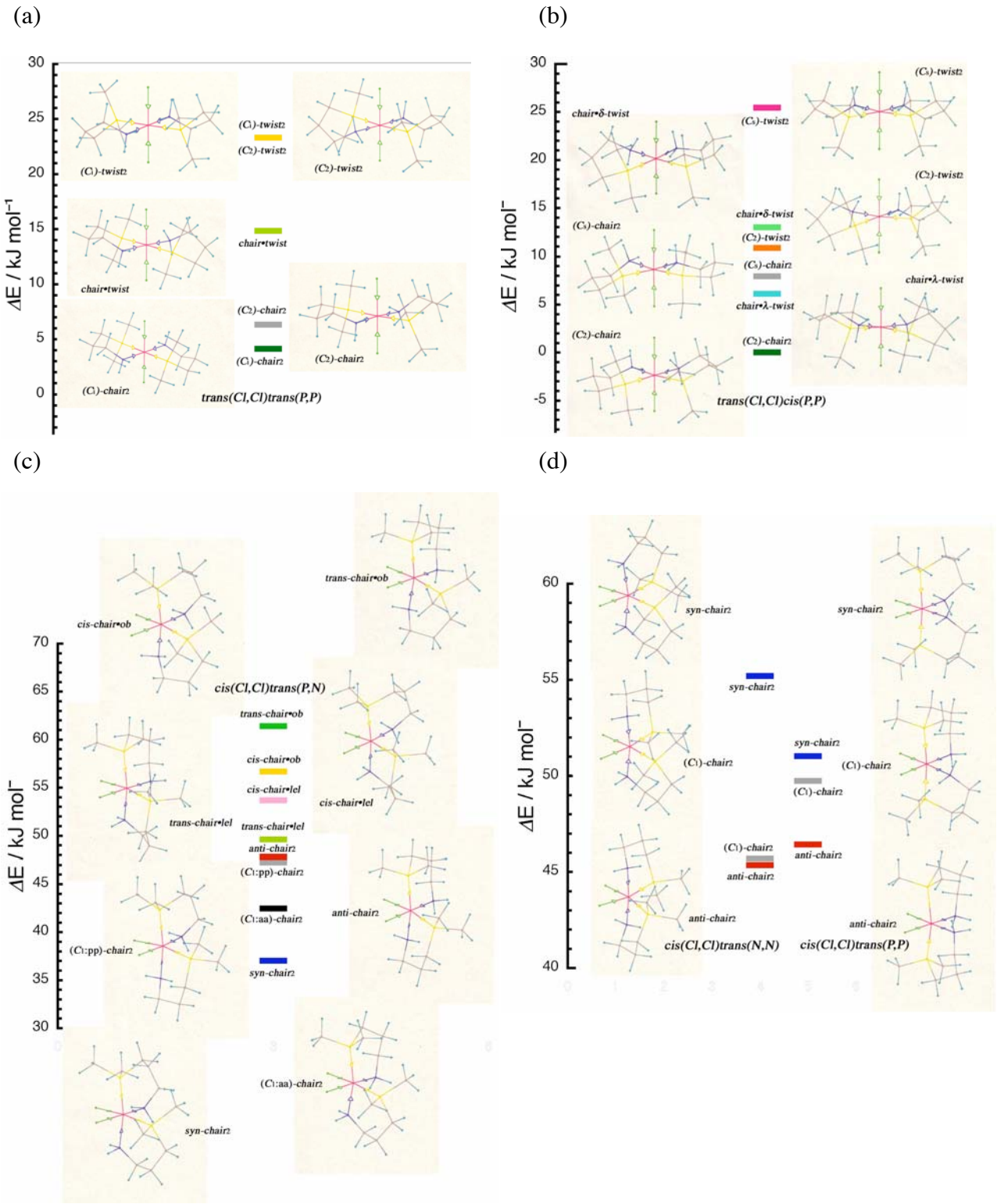


Fig. S4 The optimized structures and the relative energies of some isomers and conformers of $[CoCl_2(pdmp)_2]^+$.

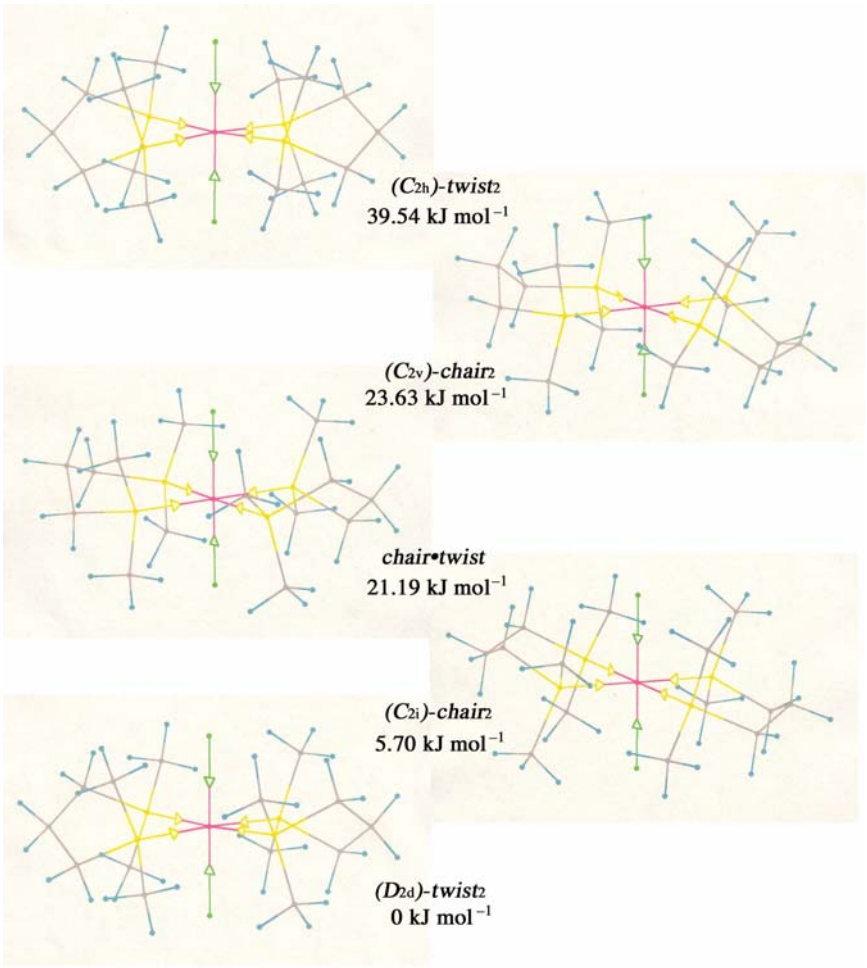


Fig. S5 The optimized structures and the relative energies of some conformers of *trans*-$[CoCl_2(dmpp)_2]^+$.

Table S2. Comparison of structural parameters (Å, °) of $[Co(en)_2(pdmp)]^{3+}$ obtained by X-ray analysis of compound **5** with those resulted from the DFT optimum geometry calculation for the *trans(lel,chair)-lel•ob•chair* conformer.

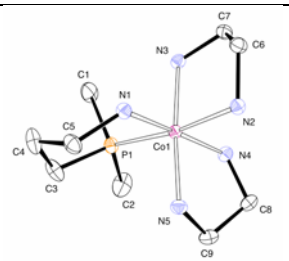
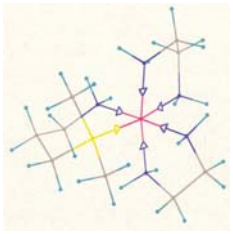
	 X-ray	 DFT calculation
Co1–P1	2.2455(10)	2.431
Co1–N1	1.992(2)	2.083
Co1–N2	2.036(2)	2.167
Co1–N3	1.975(2)	2.062
Co1–N4	1.989(2)	2.061
Co1–N5	1.995(2)	2.049
P1–Co1–N1	89.95(9)	87.91
N2–Co1–N3	83.52(9)	81.68
N4–Co1–N5	83.98(10)	83.16

Table S3. Comparison of structural parameters (Å, °) of *trans(Cl,Cl)cis(P,P)*- $[CoCl_2(pdmp)_2]^+$ obtained by X-ray analysis of compound **1** with those resulted from the DFT optimum geometry calculation for the (C_2)-$chair_2$ conformer.

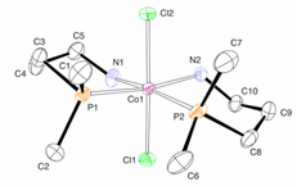
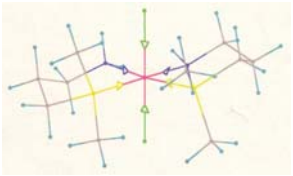
	 X-ray	 DFT calculation
Co1–Cl1	2.252(2)	2.303
Co1–Cl2	2.246(2)	2.303
Co1–P1	2.225(2)	2.319
Co1–P2	2.223(2)	2.315
Co1–N1	2.053(3)	2.128
Co1–N2	2.049(3)	2.138
P1–Co1–N1	89.58(9)	91.01
P2–Co1–N2	88.33(10)	89.62

Table S4. Comparison of structural parameters (Å, °) of *syn-chair*$_2$*-trans(P,N)*-[Co(acac)(pdmp)$_2$]$^{2+}$ obtained by X-ray analysis of compound **7a** with those resulted from the DFT optimum geometry calculation for *syn-chair*$_2$*-cis(Cl,Cl)trans(P,N)*- [CoCl$_2$(pdmp)$_2$]$^+$.

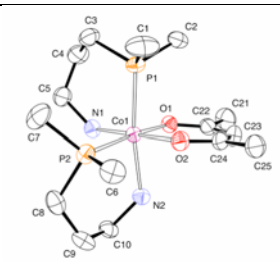
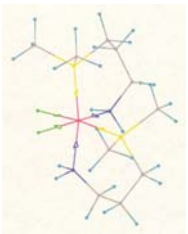
		
	X-ray	DFT calculation
Co1–P1	2.2233(12), 2.2170(11)	2.293
Co1–P2	2.2383(12), 2.2352(12)	2.329
Co1–O1 (–Cl1)	1.938(2), 1.928(2)	2.303
Co1–O2 (–Cl2)	1.901(3), 1.902(2)	2.384
Co1–N1	1.975(3), 1.979(3)	2.076
Co1–N2	2.060(3), 2.062(3)	2.136
P1–Co1–N1	95.54(10), 92.95(9)	95.34
P2–Co1–N2	89.36(9), 87.41(9)	89.93
O1–Co1–O2	93.66(12), 93.51(11)	

Table S5. Comparison of structural parameters (Å, °) of *trans-chair•lel-trans(P,N)*-[Co(dtc)(pdmp)$_2$]$^{2+}$ obtained by X-ray analysis of compound **10'** with those resulted from the DFT optimum geometry calculation for *trans-chair•lel-cis(Cl,Cl)trans(P,N)*- [CoCl$_2$(pdmp)$_2$]$^+$.

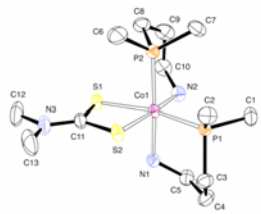
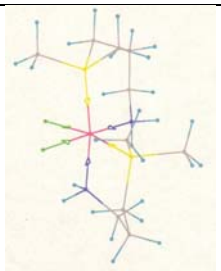
		
	X-ray	DFT calculation
Co1–P1	2.2393(6)	2.346
Co1–P2	2.2327(7)	2.310
Co1–S1 (–Cl1)	2.3139(8)	2.342
Co1–S2 (–Cl2)	2.2522(7)	2.304
Co1–N1	2.0614(17)	2.118
Co1–N2	2.0337(17)	2.085
P1–Co1–N1	89.40(5)	87.96
P2–Co1–N2	88.10(6)	90.92
P1–Co1–N2	100.15(6)	96.29

Table S6. Comparison of structural parameters (Å, °) of *anti-chair*$_2$*-trans(N,N)*-[Co(acac)(pdmp)$_2$]$^{2+}$ obtained by X-ray analysis of compound **7b** with those resulted from the DFT optimum geometry calculation for *anti-chair*$_2$*-cis(Cl,Cl)trans(N,N)*- [$CoCl_2$(pdmp)$_2$]$^+$.

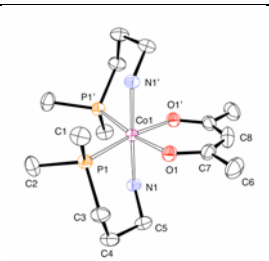
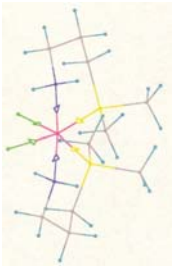
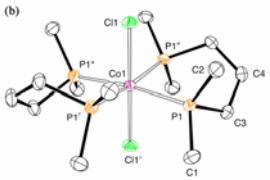
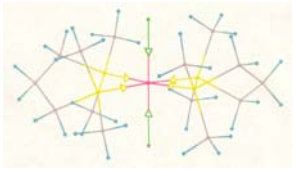
	 X-ray	 DFT calculation
Co1–P1	2.2508(7)	2.331, 2.339
Co1–O1 (–Cl1)	1.9444(18)	2.359, 2.367
Co1–N1	1.988(2)	2.066, 2.062
P1–Co1–N1	88.70(7)	87.57, 88.51
P1–Co1–P2	104.78(4)	104.76

Table S7. Comparison of structural parameters (Å, °) of *trans*-[$CoCl_2$(dmpp)$_2$]$^+$ obtained by X-ray analysis of compound **3** with those resulted from the DFT optimum geometry calculation for (D_{2d})-*twist*$_2$-*trans*-[$CoCl_2$(dmpp)$_2$]$^+$.

	 X-ray	 DFT calculation
Co1–Cl1	2.2555(9)	2.317, 2.320
Co1–P1	2.2862(7)	2.390, 2.390, 2.394, 2.395
P1–Co1–P1’	88.99(4)	88.04, 87.90