Crystal Structures of $[Co(acac)_2\{(CH_3)_2XCH_2CH_2NH_2\}]ClO_4$ (X=N, P, As; acac=2,4-Pentanedionate Ion)

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The structures of $[Co(acac)_2\{(CH_3)_2XCH_2CH_2NH_2\}]ClO_4$ (acac=2,4-pentanedionate ion, X=N (complex **1**), P (complex **2**), and As (complex **3**)) with a series of group 15 donor atoms were determined by the single-crystal X-ray diffraction method. Crystal data and final R values are: for **1**, orthorhombic, *Pba*2, $a=13.192(2)$, $b=25.504(5)$, $c=11.840(2)$ Å, $V=3984(1)$ Å^3, $D_m=1.47(2)$, $D_x=1.48$ g cm^{-3} and $Z=8$, $R=0.050$ for 2684 reflections. For **2**, monoclinic, $P2_1/c$, $a=13.953(6)$, $b=25.061(10)$, $c=12.079(7)$ Å, $\beta=92.29(6)°$, $V=4220(2)$ Å^3, $D_m=1.45(3)$, $D_x=1.45$ g cm^{-3}, $Z=8$, $R=0.084$ for 5801 reflections. For **3**, monoclinic, $C2/c$, $a=28.125(9)$, $b=13.303(1)$, $c=12.647(4)$ Å, $\beta=115.41(4)°$, $V=4274(2)$ Å^3, $D_m=1.50(3)$, $D_x=1.54$ g cm^{-3}, $Z=8$, $R=0.051$ for 3698 reflections. All the complex ions have a similar structure, forming a distorted octahedron with 4O, N, and X donor atoms. The Co–X bond lengths are av. 2.026(8) Å for **1**, av. 2.192(3) Å for **2**, and 2.302(1) Å for **3**. The Co–O bond lengths trans to X are av. 1.886(6) Å for **1**, av. 1.950(5) Å for **2**, and 1.928(3) Å for **3**, which are longer by 0.002(6), 0.065(6) and 0.037(4) Å, respectively, than the average lengths of other three Co–O bonds (**1**: av. 1.884(6), **2**: av. 1.885(6), **3**: 1.891(4) Å).

The coordination affinity of amine, phosphine, and arsine ligands seems to be fairly different from one another towards, in particular, hard Lewis acids such as Co(III), although the donor atoms of these ligands belong to the same 15(5B) group.[1] For studying such differences, it will be useful to provide structural data of amine, phosphine and arsine complexes of the same type. In the present paper, we describe X-ray structure analyses of a series complexes of the type, $[Co(acac)_2\{(CH_3)_2XCH_2CH_2NH_2\}]ClO_4$ (acac=2,4-pentanedionate ion, X=N, P, As), and compare the Co–X bond lengths and trans influence of the X donor atoms on the Co–O bond.

Experimental

The $[Co(acac)_2\{(CH_3)_2XCH_2CH_2NH_2\}]ClO_4$ (X=N,[2] P,[3] and As[4]) complexes were prepared by methods reported previously. Crystals for X-ray studies were obtained by recrystallization from aqueous solutions.

Crystal data, experimental conditions and refinement information for X-ray analyses of $[Co(acac)_2\{(CH_3)_2NCH_2CH_2NH_2\}]ClO_4$ (**1**), $[Co(acac)_2\{(CH_3)_2PCH_2CH_2NH_2\}]ClO_4$ (**2**), and $[Co(acac)_2\{(CH_3)_2AsCH_2CH_2NH_2\}]ClO_4$ (**3**) are listed in Table 1. The X-ray intensities were measured using graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.71073$ Å) on an automatic Rigaku four-circle diffractometer AFC-5 for **1** and **3**, and AFC-5R for **2**. Absorption correction was made by the Gaussian numerical integration method.[5] For **1**, the calculations were carried out on a FACOM M780/10 computer at Keio University using the computation program system UNICS-III.[6] Systematic absences $h0l$, h odd; and $0kl$, k odd suggested the space group *Pba*2 or *Pbam*. Assuming the noncentrosymmetric space group *Pba*2, the structure was solved successfully. The positions of the heavy atoms were determined by direct methods,[7] while other non-hydrogen atoms were located by means of Fourier syntheses. Anisotropic thermal parameters were applied to all non-hydrogen atoms for the refinement. The H atoms were located on difference syntheses or calculated theoretically and the refinement was made with isotropic thermal parameters. There exist two complex ions in an asymmetric unit. However, the present structure model cannot be transferred into the space group *Pbam*.

For **2** and **3**, the calculations were carried out on a HITAC M-680H computer at the Computer Center of Institute for Molecular Science with the program system UNICS-III. The structures of these two complexes were solved by the usual heavy-atom method. For **2**, the positions of two independent Co atoms were deduced by the Patterson synthesis. All of the non-hydrogen atoms of **2** and **3** were located by the subsequent Fourier synthesis. The positions of 24 of 52 H atoms in **2** and all the H atoms in **3** were identified in the subsequent difference-Fourier maps. The structures of **2** and **3** were refined by block-diagonal least squares methods with anisotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogen atoms. The final atomic parameters are listed in Table 2.[8]

Results and Discussion

Complexes **1**, **2** and **3** have the same chemical composition except the nitrogen, phosphorus, and arsenic donor atoms, and would be appropriate for comparing trans influence of group 15 donor atoms to Co(III) from their crystal structures.

Perspective drawings of the complex ions in **1**, **2**, and **3** are presented in Figs. 1, 2, and 3, respectively. The selected bond lengths and angles are listed in Table 3. Each of the complex ions forms a distorted octahedron with 4O, N, and X (N, P, As) donor atoms. In

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Table 1. Crystal Data and Refinement Information of $[Co(acac)_2\{(CH_3)_2XCH_2CH_2NH_2\}]ClO_4$ (X=N (**1**), P (**2**), and As (**3**))

	X=N (**1**)	X=P (**2**)	X=As (**3**)
Chemical formula	$C_{14}H_{26}N_2O_8ClCo$	$C_{14}H_{26}NO_8PClCo$	$C_{14}H_{26}NO_8ClCoAs$
Formular weight	444.75	461.72	505.67
Color and shape	Purple prism	Red-purple prism	Dark-red prism
Space group and Z	$Pba2$, 8	$P2_1/c$, 8	$C2/c$, 8
Cell dimensions			
a/Å	13.192(2)	13.953(6)	28.125(9)
b/Å	25.504(2)	25.061(10)	13.303(1)
c/Å	11.840(2)	12.079(7)	12.647(4)
β/°	—	92.29(6)	115.41(4)
V/Å^3	3984(1)	4220(2)	4274(2)
D_m/g cm^{-3}	1.47(2)	1.45(3)	1.50(3)
D_x/g cm^{-3}	1.48	1.45	1.53
ν(Mo $K\alpha$)/mm^{-1}	1.03	1.05	2.49
Size of specimen/mm^3	0.20×0.50×0.60	0.46×0.70×0.32	0.35×0.20×0.15
$2\sigma_{max}$/°	55	60	60
Measured reflections	4784	10408	4082
Observed reflections (F>3σ (F))	2684	5801	3698
R value	0.050	0.084	0.051

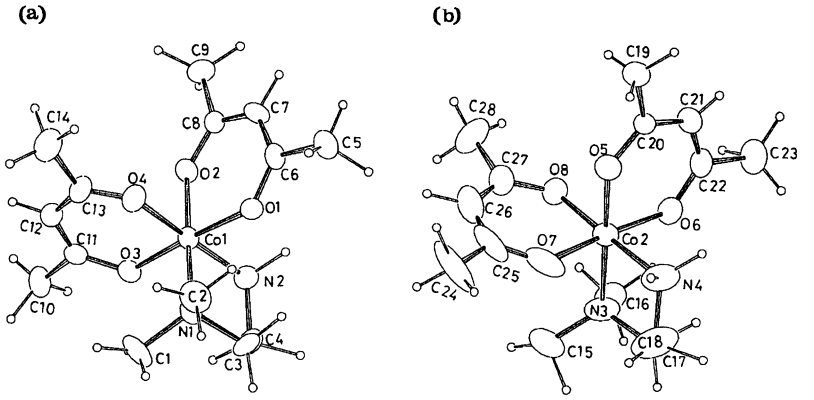

Fig. 1. Perspective views of $[Co(acac)_2\{(CH_3)_2NCH_2CH_2NH_2\}]^+$.

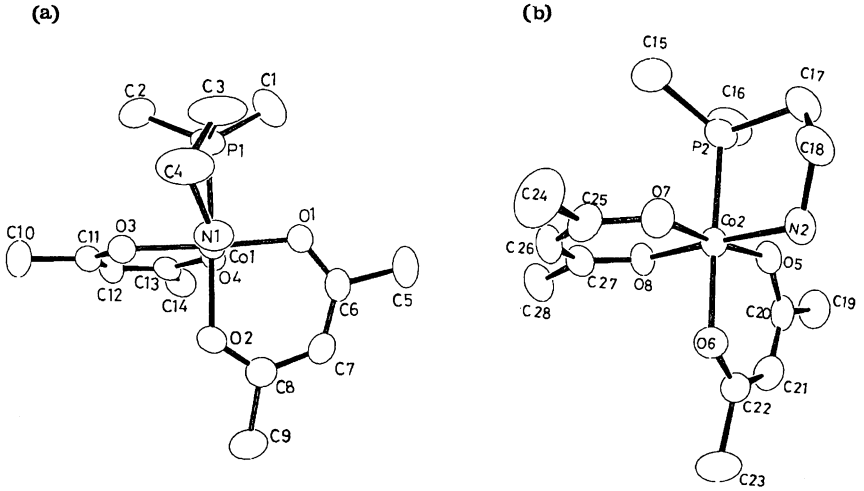

Fig. 2. Perspective views of $[Co(acac)_2\{(CH_3)_2PCH_2CH_2NH_2\}]^+$.

Table 2. Positional Parameters ($\times 10^4$) and Equivalent Isotropic Temperature Factors of [Co(acac)$_2$(Me$_2$XCH$_2$CH$_2$NH$_2$)]ClO$_4$ (X=N (**1**), P (**2**), and As (**3**))

Atom	x	y	z	B_{eq}/Å^2
[Co(acac)$_2$(Me$_2$NCH$_2$CH$_2$NH$_2$)]ClO$_4$ (**1**)				
Co(1)	7633.4(7)	6010.0(4)	4901.3(13)	3.1
Co(2)	3266.0(9)	6308.6(4)	0[a)]	3.9
Cl(1)	7716(2)	3055(1)	4299(2)	4.8
Cl(2)	844(2)	3721(1)	682(3)	6.3
N(1)	8907(5)	6179(3)	5777(6)	3.9
N(2)	8029(5)	6556(3)	3839(6)	3.9
N(3)	2981(7)	6971(3)	−898(7)	5.8
N(4)	2185(7)	6520(3)	1025(8)	6.8
O(1)	7010(4)	6530(2)	5802(5)	3.7
O(2)	6457(4)	5856(2)	4054(5)	3.7
O(3)	8306(4)	5536(2)	3925(5)	3.6
O(4)	7218(4)	5495(2)	5957(5)	4.1
O(5)	3540(4)	5713(2)	888(5)	4.4
O(6)	2283(4)	5987(2)	−895(6)	4.6
O(7)	4166(6)	6654(2)	991(6)	6.7
O(8)	4274(4)	6087(2)	−1006(5)	4.5
O(9)	8287(7)	2628(3)	3998(11)	11.4
O(10)	6871(7)	2885(5)	4479(25)	28.2
O(11)	7702(17)	3438(4)	3560(10)	24.5
O(12)	8095(11)	3307(5)	5221(15)	18.1
O(13)	280(16)	4087(5)	1150(14)	23.5
O(14)	1402(13)	3511(10)	1321(10)	28.5
O(15)	1374(13)	3813(7)	−305(8)	20.0
O(16)	197(10)	3391(5)	437(22)	27.6
C(1)	9723(7)	5781(4)	5569(10)	6.5
C(2)	8738(8)	6221(4)	6995(9)	5.8
C(3)	9248(6)	6709(4)	5319(9)	5.1
C(4)	9095(7)	6709(4)	4056(9)	4.7
C(5)	5759(7)	7077(4)	6560(9)	5.4
C(6)	6061(6)	6641(3)	5774(7)	3.7
C(7)	5350(6)	6390(3)	5102(10)	4.5
C(8)	5574(6)	6019(3)	4288(7)	3.3
C(9)	4721(7)	5795(4)	3604(9)	5.1
C(10)	8700(7)	4749(3)	3007(9)	5.1
C(11)	8189(6)	5040(3)	3962(8)	3.9
C(12)	7672(6)	4777(3)	4776(9)	4.0
C(13)	7224(7)	5008(3)	5747(8)	4.0
C(14)	6644(9)	4663(4)	6541(10)	6.4
C(15)	3753(9)	7376(4)	−715(12)	7.7
C(16)	2873(8)	6881(4)	−2116(10)	5.9
C(17)	1982(10)	7146(5)	−403(10)	8.4
C(18)	1989(11)	7085(5)	826(12)	9.8
C(19)	3503(7)	4844(4)	1498(9)	5.3
C(20)	3128(6)	5264(3)	766(8)	3.4
C(21)	2381(6)	5155(3)	−58(11)	5.0
C(22)	1985(6)	5510(4)	−798(9)	4.6
C(23)	1138(8)	5359(5)	−1561(12)	8.1
C(24)	5670(13)	6870(6)	1894(12)	12.5
C(25)	5140(10)	6617(4)	968(10)	7.7
C(26)	5636(7)	6355(4)	86(12)	7.3
C(27)	5211(7)	6107(4)	−779(10)	5.8
C(28)	5877(8)	5821(5)	−1673(12)	8.4

a) This parameter was used to define the origin of the unit cell along z and is listed without esd.

Table 2. (Continued)

Atom	x	y	z	B_{eq}/Å^2
[Co(acac)$_2$(Me$_2$PCH$_2$CH$_2$NH$_2$)]ClO$_4$ (**2**)				
Co(1)	425(1)	1364.8(4)	2559(1)	4.0
Co(2)	4681(1)	3674.2(3)	2756(1)	3.9
Cl(1)	4179(2)	9264(1)	6439(2)	6.6
Cl(2)	687(2)	5726(1)	6850(2)	7.0
P(1)	−890(2)	1151(1)	3388(2)	5.3
P(2)	5915(2)	3933(1)	3800(2)	5.6
O(1)	1062(4)	875(2)	3508(4)	4.7
O(2)	1552(4)	1534(2)	1723(4)	5.1
O(3)	−281(4)	1807(2)	1581(4)	5.3
O(4)	797(4)	1907(2)	3588(4)	4.5
O(5)	3961(4)	4142(2)	3610(4)	5.0
O(6)	5476(4)	3257(2)	1898(4)	5.5
O(7)	4325(4)	3123(2)	3736(4)	4.6
O(8)	3623(4)	3465(2)	1753(4)	4.7
O(9)	4047(15)	8852(5)	7169(10)	13.2
O(10)	3444(16)	9177(16)	5609(18)	21.2
O(11)	3818(14)	9709(4)	6923(22)	17.1
O(12)	4985(9)	9340(9)	5825(12)	13.6
O(13)	1232(8)	5308(5)	6458(14)	12.4
O(14)	−2(12)	5543(10)	7575(21)	16.0
O(15)	1257(13)	6076(8)	7501(15)	14.6
O(16)	232(31)	5986(13)	6037(12)	25.7
N(1)	98(5)	792(3)	1518(6)	5.7
N(2)	4995(5)	4257(3)	1756(5)	5.3
C(1)	−749(12)	950(5)	4820(11)	9.2
C(2)	−1809(7)	1653(5)	3326(10)	7.2
C(3)	−1266(9)	557(6)	2586(12)	9.3
C(4)	−922(9)	643(6)	1453(10)	8.9
C(5)	2316(10)	413(4)	4434(10)	7.9
C(6)	1960(6)	802(3)	3559(6)	5.0
C(7)	2610(6)	1036(3)	2886(7)	5.5
C(8)	2372(6)	1384(3)	2019(6)	5.1
C(9)	3153(7)	1623(5)	1329(9)	7.1
C(10)	−976(9)	2585(7)	809(12)	9.7
C(11)	−364(6)	2322(4)	1707(7)	5.8
C(12)	74(7)	2611(3)	2565(8)	6.0
C(13)	632(6)	2408(3)	3405(7)	5.1
C(14)	1121(8)	2777(4)	4227(9)	6.7
C(15)	6920(8)	3480(5)	3869(11)	8.2
C(16)	5646(11)	4110(7)	5231(9)	9.4
C(17)	6258(8)	4540(4)	3105(10)	7.6
C(18)	5990(8)	4455(4)	1892(9)	7.4
C(19)	2612(9)	4545(4)	4363(10)	7.8
C(20)	3048(6)	4180(3)	3509(7)	5.1
C(21)	2465(6)	3928(4)	2750(8)	5.8
C(22)	2776(5)	3596(3)	1919(7)	5.0
C(23)	2042(7)	3331(5)	1120(9)	7.6
C(24)	6249(11)	2503(7)	1222(13)	10.2
C(25)	5582(6)	2747(4)	2038(7)	5.7
C(26)	5153(7)	2448(3)	2819(8)	6.0
C(27)	4554(6)	2630(3)	3606(7)	5.0
C(28)	4093(8)	2248(4)	4384(9)	6.9

each unit cell of **1** and **2**, there are two crystallographically independent complex ions, but they are quite similar in geometries and chemically equivalent. Table 4 gives the average bond lengths around the Co(III) ion. The Co–X bond length increases in the order of X=N<P<As. The Co–N(CH$_3$)$_2$bond in **1** is

Table 2. (Continued)

Atom	x	y	z	B_{eq}/Å^2
$[Co(acac)_2(Me_2AsCH_2CH_2NH_2)]ClO_4$ (**3**)				
As	3798.7(2)	3824(1)	4446(1)	3.5
Co	3563.9(3)	2351(1)	3380(1)	3.1
Cl	5674(1)	2757(1)	5011(1)	4.6
O(1)	4065(1)	1712(3)	4725(2)	4.0
O(2)	3399(1)	1183(3)	2377(2)	3.9
O(3)	3099(1)	3096(3)	2058(1)	3.6
O(4)	3045(1)	1970(3)	3897(2)	3.9
O(5)	6031(2)	2287(5)	4636(2)	8.3
O(6)	5933(3)	2868(5)	6245(2)	9.3
O(7)	5526(2)	3718(4)	4463(3)	6.8
O(8)	5225(2)	2168(5)	4717(3)	10.7
N	4115(2)	2707(4)	2887(3)	3.7
C(1)	4190(3)	3734(6)	6128(5)	6.5
C(2)	3274(3)	4833(5)	4201(5)	5.7
C(3)	4287(3)	4350(5)	3873(4)	5.5
C(4)	4198(2)	3796(5)	2761(4)	4.7
C(5)	4600(3)	453(6)	5947(5)	6.6
C(6)	4183(2)	784(5)	4772(3)	4.2
C(7)	3974(3)	105(5)	3857(5)	5.3
C(8)	3603(2)	325(4)	2725(4)	3.9
C(9)	3406(3)	−496(5)	1818(4)	5.7
C(10)	2308(2)	3658(5)	568(4)	5.3
C(11)	2602(2)	3061(4)	1669(5)	3.5
C(12)	2330(2)	2551(5)	2195(6)	4.3
C(13)	2555(2)	2056(4)	3266(3)	3.6
C(14)	2201(3)	1604(5)	3741(4)	5.3

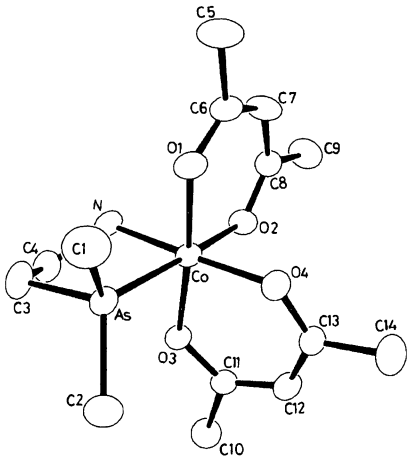

Fig. 3. A perspective view of $[Co(acac)_2\{(CH_3)_2As\text{-}CH_2CH_2NH_2\}]^+$.

longer by ca. 0.08 Å than the Co–NH_2 bond and similar to that in $[Co(tp)_2\{(CH_3)_2NCH_2CH_2NH_2\}]ClO_4$ (2.022(4) Å, tp=tropolonate ion).[9] The elongation of the Co–$N(CH_3)_2$ bond may be attributed to the bulkiness of the tertiary amine donor group.[10] Both Co–P in **2** (av. 2.192(2) Å) and Co–As in **3** (av. 2.302(1) Å) bond lengths are fairly short compared, respectively, with those reported for Co(III) complexes with dimethyl-phosphino[11] and -arsino[12] donor groups. The Co–P and Co–As bond lenghts usually found are around 2.25 and 2.35 Å, respectively.

Table 3. Selected Bond Distances (l/Å) and Bond Angles (ϕ/°) of $[Co(acac)_2(Me_2XCH_2CH_2NH_2)]\text{-}ClO_4$ (X=N (**1**), P (**2**), and As (**3**))

$[Co(acac)_2(Me_2NCH_2CH_2NH_2)]ClO_4$ (**1**)			
Co(1)–N(1)	2.021(7)	Co(1)–N(2)	1.947(7)
Co(1)–O(1)	1.890(6)	Co(1)–O(2)	1.889(6)
Co(1)–O(3)	1.893(6)	Co(1)–O(4)	1.894(6)
N(1)–C(1)	1.50(1)	N(1)–C(2)	1.46(1)
N(1)–C(3)	1.53(1)	Co(2)–N(3)	2.031(8)
Co(2)–N(4)	1.948(9)	Co(2)–O(5)	1.882(6)
Co(2)–O(6)	1.864(6)	Co(2)–O(7)	1.888(7)
Co(2)–O(8)	1.873(6)	N(3)–C(15)	1.47(1)
N(3)–C(16)	1.47(1)	N(3)–C(17)	1.51(2)
N(1)–Co(1)–N(2)	87.5(3)	N(1)–Co(1)–O(1)	85.6(3)
N(1)–Co(1)–O(2)	178.8(3)	N(1)–Co(1)–O(3)	93.4(3)
N(1)–Co(1)–O(4)	92.9(3)	N(2)–Co(1)–O(1)	88.8(3)
N(2)–Co(1)–O(2)	91.5(3)	N(2)–Co(1)–O(3)	86.6(3)
N(2)–Co(1)–O(4)	178.1(3)	O(1)–Co(1)–O(2)	95.1(2)
O(1)–Co(1)–O(3)	175.1(2)	O(1)–Co(1)–O(4)	89.3(2)
O(2)–Co(1)–O(3)	85.9(2)	O(2)–Co(1)–O(4)	88.2(2)
O(3)–Co(1)–O(4)	95.5(2)	Co(1)–N(1)–C(1)	111.6(6)
Co(1)–N(1)–C(2)	113.3(6)	Co(1)–N(1)–C(3)	104.6(5)
C(1)–N(1)–C(2)	108.8(7)	C(1)–N(1)–C(3)	109.2(7)
C(2)–N(1)–C(3)	109.3(7)	N(3)–Co(2)–N(4)	87.7(4)
N(3)–Co(2)–O(5)	177.5(3)	N(3)–Co(2)–O(6)	86.5(3)
N(3)–Co(2)–O(7)	93.1(3)	N(3)–Co(2)–O(8)	92.8(3)
N(4)–Co(2)–O(5)	90.9(3)	N(4)–Co(2)–O(6)	88.1(3)
N(4)–Co(2)–O(7)	86.8(4)	N(4)–Co(2)–O(8)	177.9(3)
O(5)–Co(2)–O(6)	95.5(2)	O(5)–Co(2)–O(7)	84.8(3)
O(5)–Co(2)–O(8)	88.6(2)	O(6)–Co(2)–O(7)	174.9(3)
O(6)–Co(2)–O(8)	90.0(3)	O(7)–Co(2)–O(8)	95.2(3)
Co(2)–N(3)–C(15)	112.3(7)	Co(2)–N(3)–C(16)	113.7(6)
Co(2)–N(3)–C(17)	101.8(7)	C(15)–N(3)–C(16)	108.9(8)
C(15)–N(3)–C(17)	109.9(8)	C(16)–N(3)–C(17)	110.1(9)

Except the Co–O bond trans to X, both lengths of the Co–NH_2 (1.948(8)—1.956(5) Å) and the Co–O (1.870(6)—1.900(4) Å) bonds are very similar among the complexes. The Co–O bond length trans to X increases in the order of **1**<**3**<**2**. The difference between this Co–O bond length and the average length for three other Co–O bonds is 0.002(6) Å for **1**, 0.065(6) Å for **2**, and 0.037(4) Å for **3**. The elongation of the Co–O bonds trans to P and As is attributable to the trans influence of these donor atoms, and the magnitude of trans influence of group 15 donor atoms indicates to be P>As>N in these Co(III) complexes. The sequence for the ligand field strength is also reported to be P>As>N for Co(III).[4]

The N–Co–X chelate angle decreases with the lengthening Co–X bond (**1**: av. 87.6(4)°, **2**: av. 86.2(2)°, **3**: 85.1(1)°). The chelate ring in **1** takes a gauche conformation with the dihedral angle, N–C–C–X of av. 56.0(2)°, while that in **3** is nearly an envelope conformation and the dihedral angle is 41.4(2)°. The conformation in **2** is intermediate between them with the dihedral angle of av. 49.7(5)°. The chelate ring tends to become flat as the Co–X and X–C bonds lengthen (Table 4 and Fig. 4).

Table 3. (Continued)

$[Co(acac)_2(Me_2PCH_2CH_2NH_2)]ClO_4$ (**2**)			
Co(1)–P(1)	2.192(3)	Co(1)–N(1)	1.946(7)
Co(1)–O(1)	1.877(5)	Co(1)–O(2)	1.952(5)
Co(1)–O(3)	1.872(5)	Co(1)–O(4)	1.897(5)
Co(2)–P(2)	2.192(3)	Co(2)–N(2)	1.955(7)
Co(2)–O(5)	1.877(5)	Co(2)–O(6)	1.947(5)
Co(2)–O(7)	1.868(6)	Co(2)–O(8)	1.896(5)
P(1)–C(1)	1.82(1)	P(1)–C(2)	1.79(1)
P(1)–C(3)	1.84(1)	P(2)–C(15)	1.80(1)
P(2)–C(16)	1.84(1)	P(2)–C(17)	1.81(1)
P(1)–Co(1)–N(1)	86.4(2)	P(1)–Co(1)–O(1)	86.9(2)
P(1)–Co(1)–O(2)	175.8(2)	P(1)–Co(1)–O(3)	90.2(2)
P(1)–Co(1)–O(4)	95.1(2)	N(1)–Co(1)–O(1)	90.3(3)
N(1)–Co(1)–O(2)	89.9(3)	N(1)–Co(1)–O(3)	85.7(3)
N(1)–Co(1)–O(4)	177.4(3)	O(1)–Co(1)–O(2)	94.9(2)
O(1)–Co(1)–O(3)	175.2(2)	O(1)–Co(1)–O(4)	87.7(2)
O(2)–Co(1)–O(3)	87.7(2)	O(2)–Co(1)–O(4)	88.7(2)
O(3)–Co(1)–O(4)	96.4(2)	Co(1)–P(1)–C(1)	115.9(4)
Co(1)–P(1)–C(2)	114.9(4)	Co(1)–P(1)–C(3)	100.5(4)
C(1)–P(1)–C(2)	106.8(6)	C(1)–P(1)–C(3)	107.4(6)
C(2)–P(1)–C(3)	111.3(5)	P(2)–Co(2)–N(2)	86.7(2)
P(2)–Co(2)–O(5)	85.7(2)	P(2)–Co(2)–O(6)	176.5(2)
P(2)–Co(2)–O(7)	90.8(2)	P(2)–Co(2)–O(8)	94.4(2)
N(2)–Co(2)–O(5)	90.7(3)	N(2)–Co(2)–O(6)	90.1(3)
N(2)–Co(2)–O(7)	85.5(3)	N(2)–Co(2)–O(8)	177.7(3)
O(5)–Co(2)–O(6)	95.8(2)	O(5)–Co(2)–O(7)	175.0(2)
O(5)–Co(2)–O(8)	87.3(2)	O(6)–Co(2)–O(7)	87.6(2)
O(6)–Co(2)–O(8)	88.9(2)	O(7)–Co(2)–O(8)	96.6(2)
Co(2)–P(2)–C(15)	115.7(4)	Co(2)–P(2)–C(16)	115.1(5)
Co(2)–P(2)–C(17)	101.4(4)	C(15)–P(2)–C(16)	107.4(7)
C(15)–P(2)–C(17)	109.4(6)	C(16)–P(2)–C(17)	107.5(6)
$[Co(acac)_2(Me_2AsCH_2CH_2NH_2)]ClO_4$ (**3**)			
Co–As	2.302(1)	Co–N	1.956(5)
Co–O(1)	1.878(3)	Co–O(2)	1.928(3)
Co–O(3)	1.896(3)	Co–O(4)	1.900(4)
As–C(1)	1.930(5)	As–C(2)	1.915(8)
As–C(3)	1.933(8)		
As–Co–N	85.1(1)	As–Co–O(1)	86.5(1)
As–Co–O(2)	173.6(1)	As–Co–O(3)	89.3(1)
As–Co–O(4)	95.4(1)	N–Co–O(1)	90.5(2)
N–Co–O(2)	89.1(2)	N–Co–O(3)	86.1(2)
N–Co–O(4)	177.9(2)	O(1)–Co–O(2)	96.1(1)
O(1)–Co–O(3)	174.9(2)	O(1)–Co–O(4)	87.5(2)
O(2)–Co–O(3)	87.7(1)	O(2)–Co–O(4)	90.5(2)
O(3)–Co–O(4)	95.9(2)	Co–As–C(1)	118.4(3)
Co–As–C(2)	119.5(2)	Co–As–C(3)	99.2(2)
C(1)–As–C(2)	104.8(3)	C(1)–As–C(3)	105.9(3)
C(2)–As–C(3)	107.8(3)		

The average C–X–C bond angle slightly decreases in the order of **1** (109.4(9)°)>**2** (108.3(7)°)>**3** (106.2(3)°). For free XH_3 and their derivatives XR_3 (X=N, P, As), the bond angles are known to decrease in the same order N>P>As, and the decrease can be understood in terms of an increase in the p character for the X–H(R) bond.[13] The X donor groups in the complexes seem to retain these bonding characters of free ligands.

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Table 4. Bond Distances (l/Å) around the Co(III) and X in $[Co(acac)_2\{(CH_3)_2XCH_2CH_2NH_2\}]^+$ (Average Values for X=N and P)

	X=N	X=P	X=As
Co–X	2.026(8)	2.192(2)	2.302(1)
Co–NH_2	1.948(8)	1.951(7)	1.956(5)
(1) Co–O trans to X	1.886(6)	1.950(5)	1.928(3)
(2) Co–O trans to NH_2	1.884(6)	1.897(5)	1.900(4)
(3) Co–O trans to O	1.877(6)	1.870(6)	1.878(3)
	1.891(7)	1.877(5)	1.896(3)
(4) av. of (**2**) and (**3**)	1.884(6)	1.885(6)	1.891(4)
Δ=(1)−(4)	0.002(6)	0.065(6)	0.037(4)
X–C (averaged)	1.49(1)	1.82(1)	1.926(7)

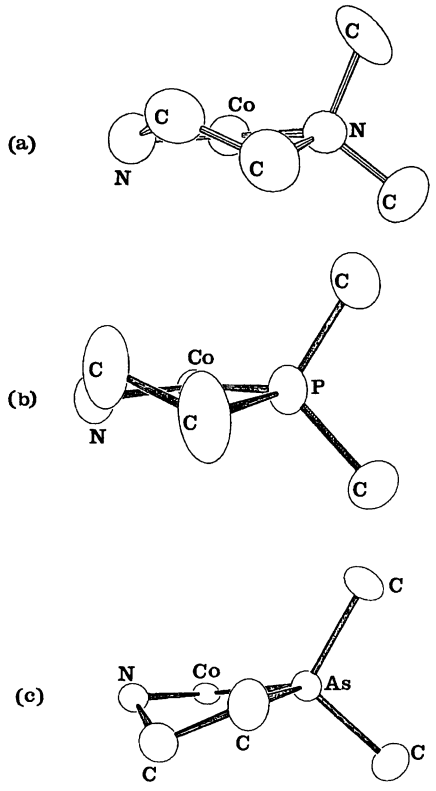

Fig. 4. Conformations of the $(CH_3)_2XCH_2CH_2NH_2$ chelate ring, (a) X=N, (b) X=P, and (c) X=As.

References

1) C. A. McAuliffe and W. Levason, "Phosphine, Arsine, and Stibine Complexes of the Transition Elements," Elsevier, Amsterdam (1979).

2) Y. Ouyang, M. Kojima, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **57**, 3574 (1984).

3) K. Kashiwabara, I. Kinoshita, T. Ito, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **54**, 725 (1981).

4) K. Nemoto, M. Kita, M. Kojima, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **62**, 1517 (1989).

5) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**,

180 (1957).

6) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, **55**, 69 (1979).

7) P. Main, S. E. Hull, L. Lessinger, G. Germain, J. -P. Declercq, and M. M. Woolfson, "MULTAN78. A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data," Univs. of York, England, and Louvain, Belgium (1978).

8) Tables of coordinates of hydrogen atoms, the anisotropic thermal parameters of the non-hydrogen atoms, and the observed and calculated structure factors are kept as Document No. 66020 at the Office of the Editor of Bull. Chem. Soc. Jpn.

9) M. Kojima, Q. Ma, T. Miyamoto, S. Ohba, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **65**, 1572 (1992).

10) A. L. Seligson and W. C. Trogler, *J. Am. Chem. Soc.*, **113**, 2520 (1991).

11) I. Kinoshita, K. Kashiwabara, J. Fujita, K. Matsumoto, and S. Ooi, *Bull. Chem. Soc. Jpn.*, **54**, 2683 (1981); S. Ohba, Y. Saito, T. Ohishi, K. Kashiwabara, and J. Fujita, *Acta Crystallogr., Sect. C*, **39**, 49 (1983); T. Ohishi, S. Ohba, K. Kashiwabara, Y. Saito, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **57**, 877 (1984); T. Ohishi, K. Kashiwabara, J. Fujita, S. Ohba, T. Ishii, and Y. Saito, *Bull. Chem. Soc. Jpn.*, **59**, 385 (1986); M. Kita, A. Okuyama, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **63**, 1994 (1990); M. Kita, M. Okuno, K Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **65**, 3402 (1992).

12) P. K. Bernstein, G. A. Rodley, R. Marsh, and H. B. Gray, *Inorg. Chem.*, **11**, 3040 (1972); H. C. Jewiss, W. Levason, and M. Webster, *Inorg. Chem.*, **25**, 1997 (1986); K. Simonsen, M. Hamada, N. Suzuki, M. Kojima, S. Ohba, F. Galsbøl, Y. Saito, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **63**, 2904 (1990).

13) N. N. Greenwood and A. Earnshaw, "Chemistry of the Elements," Pergamon Press, Oxford (1984), p. 650.