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Redox potentials of a series of bis(2,4-pentanedionato)cobalt(III) complexes containing amine, phosphine, arsine, or their hybrid donor didentate ligands. σ and π Contributions in the Co^{III}—N, —P and —As bonding

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Abstract—Reduction ($E_{1/2}$(red)) and oxidation potentials ($E_{1/2}$(ox)) of $[Co(acac)_2(L)]^+$ (acac = 2,4-pentanedionate) complexes containing an N—N, N—N′, N′—N′, N—P, P—P, N—As, or As—As′ didentate ligand as L(N = —CH_2NH_2; N′ = —CH_2NMe_2; P = —CH_2PMe_2; As = —CH_2AsMe_2; As′ = —$CH_2CH_2AsMe_2$) were determined by electrochemical measurements. The $E_{1/2}$(red) values which reflect the $d\sigma^*$(Co) orbital (homo) energy shift negatively in the following order: (i) L = N′—N′ > N′—N > N—N; (ii) L = N′—N > As—N > P—N; and (iii) L = N′—N′ > As—As′ > P—P. The $E_{1/2}$(ox) values shift positively in the following order: L = P—P, As—As′ < P—N, As—N < N—N, N—N′, N′—N′. This order suggests that the $d\pi$(Co) orbital is more destabilized by the phosphine or arsine ligands than the amine ones. © 1997 Elsevier Science Ltd

Keywords: redox potentials of Co^{III} complexes; σ and π contributions; Co^{III}—N, —P and —As bonding; trans influence; geometry of donor groups; ligand field strength.

We have been interested in cobalt(III)-phosphine complexes which are composed of typical Lewis hard acid and soft bases, and the molecular structures of $[Co(acac)_2(Me_2XCH_2CH_2NH_2)]ClO_4$ (X = N, P or As) were reported in a previous paper [1]. These complexes are different only in the X of 5B(15) group atoms, and they give a suitable system for comparative studies on the coordination properties of these 5B donor groups towards a Co^{III} ion (bond distances and angles, their *trans* influences, bonding properties etc). We have also reported the redox potentials of cobalt(III) mixed-ligand complexes with sulfur, phosphorous, and nitrogen donor atoms, and a good linear relationship was observed between the potential difference, [$E_{1/2}$(ox)-$E_{1/2}$(red)] and the first *d*-*d* transition energies of the complexes [2]. The linear relationship suggests that the $E_{1/2}$(ox) and $E_{1/2}$(red) values nicely reflect the orbital energies of $d\sigma^*$(Co) (lumo) and $d\pi$(Co) (homo), respectively.

Here, we report the electrochemical investigations for seven cobalt(III) complexes containing amine, phosphine and arsine donor ligands to examine the bonding nature between the —XMe_2(X = N, P, or As) donor groups and the Co^{III} center. The present results will give a quantitative estimation for the σ and π contributions in the cobalt^{III}-amine, -phosphine and -arsine complexes.

EXPERIMENTAL

The complexes measured were prepared by the literature methods: $[Co(acac)_2(L)]ClO_4$(L = N′—N [3], N—N′ [3], N′—N′ [3], P—N [4], P—P [5], As—N [6] and As—As′ [7]. The rotating disk electrode (RDE) voltammetry employed in the present study were recorded with the same apparatus and in the

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same manner as described previously [2]. Absorption spectra in CH_3CN solutions were measured on a Hitachi U3400 spectrophotometer. The optimal geometries of free $X(CH_3)_3$ ($X = N$, P, and As) were determined by RHF calculations using the Mulliken program [8] (for $X = N$ and P with 6-31G*, and for $X = As$ with STO-3G basis sets).

RESULTS AND DISCUSSION

Table 1 shows the $E_{1/2}$(red) and $E_{1/2}$(ox) values and the first *d—d* transition energies for seven [Co(acac)$_2$L)]ClO$_4$ complexes. The quasi-reversible waves with small ($E_{3/4}-E_{1/4}$) values on oxidation or ($E_{1/4}-E_{3/4}$) ones on reduction were obtained by RDE voltammetry technique. Although the observed (apparent) first *d–d* bands of some phosphine and arsine complexes are split as indicated, the lower component or the apparent peak energies are approximately same as the differences ΔE(redox) ($\equiv e[E_{1/2}(\text{ox}) - E_{1/2}(\text{red})]$) for the present cobalt(III) complexes.

Figure 1 shows the visualization of the $E_{1/2}$(ox) and $E_{1/2}$(red) values of the complexes which are grouped into three; a, b, and c. The $E_{1/2}$(red) values in Fig. 1(a) dramatically decrease by the stepwise substitutions from —NH$_2$ to —NMe$_2$, which indicates that the σ-type interaction of the ligands with the Co center is much greater in the primary amine than the tertiary one. The weakening of such an amine's σ-donation ability by substituting with a methyl group may be caused by the steric effect. On the other hand, the $E_{1/2}$(ox) values in Fig. 1(a) are invariant, which suggests that the $d\pi$(Co) orbital energy is not changed whichever the amine type is primary or tertiary. Thus, no π interaction between $d\pi$(Co) and the aliphatic amines exist; the $d\pi$(Co) orbital being essentially nonbonding to the aliphatic amines. The decrease of the first *d—d* band energies of the cobalt(III) complexes with the substitution from —NH$_2$ to —NMe$_2$ is well known [3], and now we clarify it visually; it is mainly caused by the decrease of the σ interaction of amines with the Co^{III} center.

The $E_{1/2}$(ox) and $E_{1/2}$(red) values of [Co(acac)$_2$(Me$_2$XCH$_2$CH$_2$NH$_2$)]ClO$_4$ ($X = N$, P, or As), are shown in Fig. 1(b). The first *d–d* transition bands around 20 000 cm^{-1} are shifted as the following order: $X = P$ (20 200 cm^{-1}) > As (18 700 cm^{-1}) > N (17 700 cm^{-1}). The *trans* influence in their crystal structures, which can be defined as the difference between the bond distances of the Co—O *trans* to X and the Co—O *trans* to O, decreases in the following order: $X = P$ (0.076(11) Å) > As (0.041(4) Å) > N (0.015(6) Å) [1]. This order is coincident with the $E_{1/2}$(red) order of the complexes: $X = P$ (−1.04 V) < As(−0.86 V) < N(−0.78 V). Since the $E_{1/2}$(red) value reflects the $d\sigma^*$(Co) orbital energy, the agreement between the *trans* influence order and the $E_{1/2}$(red) one demonstrates that both the orders are associated with the σ interaction between the —XMe$_2$ group and the Co^{III} center. The change of the $E_{1/2}$(red) values of the complexes in Fig. 1(c), which contain a symmetrical X—X ligand, becomes approximately twice to the corresponding ones in Fig. 1(b): $X = P$ (−1.16 V) < As(−0.86 V) < N (−0.69 V) as shown in Fig. 1(c). Our consideration on the σ interaction is confirmed by this observation: the changes in Fig. 1(c) are approximately twice those in Fig. 1(b).

The RHF calculation (Mulliken) gives that the σ donor orbital of $X(CH_3)_3$ with a symmetry under C_{3v} assumption is destabilized as the following order: −9.4 eV for $X = N$ < −8.8 eV for $X = P$ < −6.9 eV for $X = As$ and the orbitals are visualized in Fig. 2(a) which shows that the molecular orbital isosurface with 0.1 value expands in the order: N < P < As. The magnitude of the σ interaction estimated by the electrochemistry is not in agreement with the trend of the calculated orbital energies. It could cause such a disagreement to the large covalent radius (and the expanding cloud) of As atom and/or the strong π repulsion between $d\pi$(Co) and the filled π-type orbitals of As(CH$_3$)$_3$ as is mentioned in the following section.

The $E_{1/2}$(ox) values which reflect the $d\pi$(Co) orbital energy of the complexes decrease in the following order: $X = N$ (1.41 V) > P(1.29 V) $\geqslant$ As (1.26 V) in

Table 1. Redox potentials of [Co(acac)$_2$L]ClO$_4$ (L = N—N, N—N′, N′—N′, N—P, P—P, N—As, As—As′ (see text)) and their first *d—d* transition energies

	N—N	N—N′	N′—N′	N—P	P—P	N—As	As—As′
$E_{1/2}$(ox) (V)	1.41	1.41	1.44	1.29	1.20	1.26	1.21
$E_{3.4}-E_{1/4}$ (mV)	90	70	60	60	60	80	70
i_1 (mA mmol^{-1})	101	102	104	88	70	129	73
$E_{1/2}$(red) (V)	−0.95	−0.78	−0.69	−1.04	−1.16	−0.86	−0.86
$E_{1/4}-E_{3/4}$ (mV)	110	120	115	101	80	110	90
i_1 (mA mmol^{-1})	69	81	75	74	87	73	60
ΔE(redox) (eV)	2.36	2.19	2.13	2.33	2.36	2.12	2.07
σd–d^a (eV)	2.29	2.19	2.06	2.08^{sh}, 2.51	2.39^{sh}, 2.90^{sh}	2.32	2.17^{sh}, 2.47

[a] The apparent peaks or shoulders in the first *d–d* transition region. sh: shoulder.

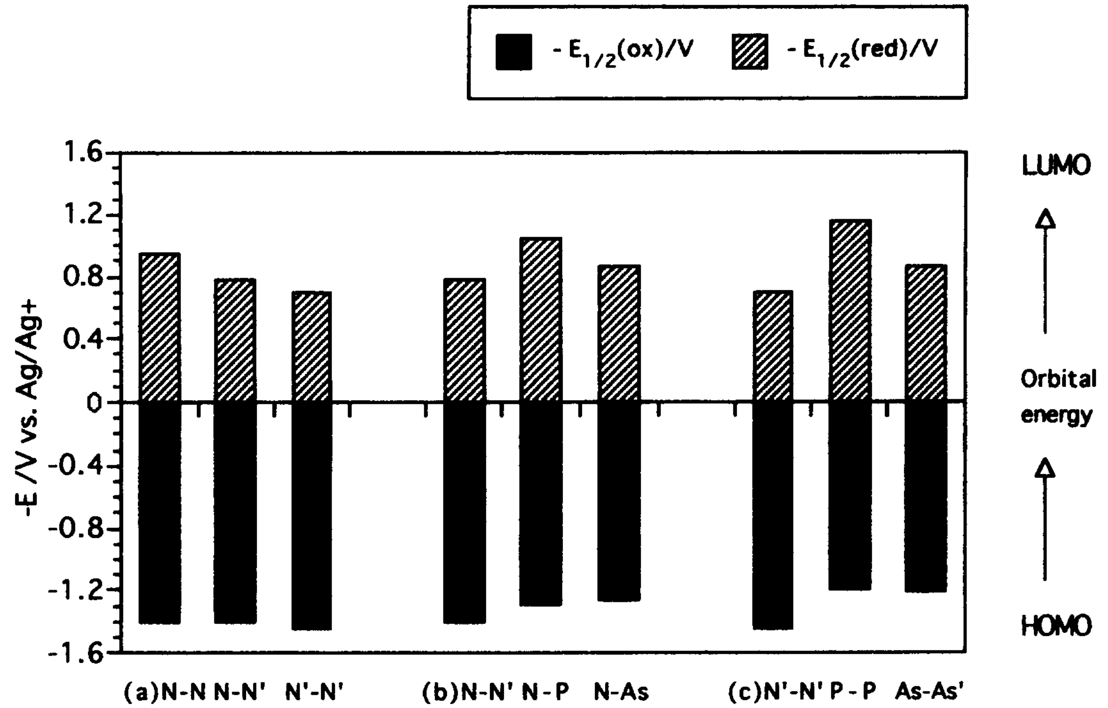
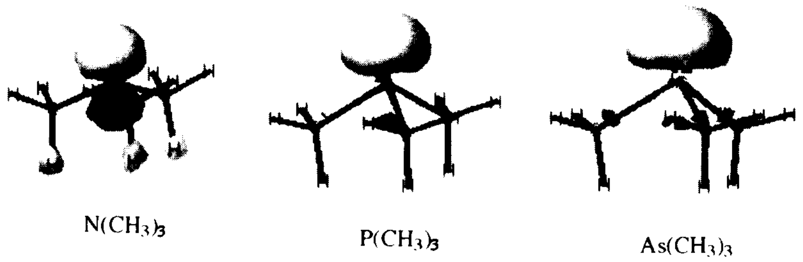


Fig. 1. Visualizing the trend of redox potentials of the three series of $[Co(acac)_2(X—Y)]^+$. In a series the change of $-E_{1/2}$(red) or $-E_{1/2}$(ox) values with opposite sign corresponds to the change of LUMO or HOMO orbital energies, respectively.

(a) **a**-type orbital (C_{3v} symmetry)



(b) one component of **e**-type orbitals (C_{3v} symmetry)

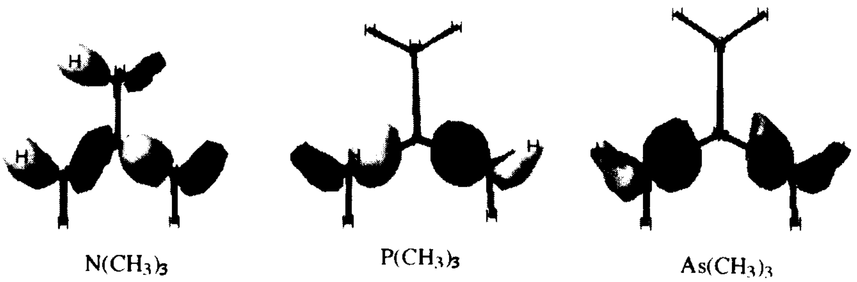


Fig. 2. Visualizing **a** and **e** orbitals of $X(CH_3)_3(X = N, P, and As)$ by Mulliken treatment.

Fig. 1(b) and X = N (1.44 V) > As (1.21 V) ⩾ P (1.20 V) in Fig. 1(c). The orders suggest that the $d\pi$(Co) orbitals of the phosphine and arsine complexes are more destabilized than those of the amine ones. In other words, the phosphine and arsine ligands act as a π donor to the Co^{III} ion. On the basis of the angular overlap model (AOM) treatment for the electronic spectra of the cobalt(III)-phosphine complexes, we obtained similar results [9]. The phosphine and arsine ligands have a filled π-type molecular orbital (e symmetry under C_{3v} approximation) composed of three P—C (or As—C) σ-bonds as shown in Fig. 2(b), which shows that the separation between the positive and negative area increases in the order : N < P < As. The filled π-type orbitals labeled **e** symmetry of the phosphine and arsine ligands can interact repulsively with the filled $d\pi$(Co) orbitals. The destabilization, however, is overcome by the strong σ-interaction mentioned above to give the strong ligand field of the —PMe_2 group. The strong covalency between the —PMe_2 group and a Co^{III} ion has been claimed in spectroscopic studies on a series of cobalt(III)-phosphine complexes [10, 11].

The energies of the occupied MOs of free XMe_3 obtained by Mulliken calculations are listed in Table 2 with the observed (by crystallography) and calculated geometrical parameters (by the Mulliken treatment). The **a** and **e** orbitals are shown in Fig. 2. The calculated optimal geometries by the Mulliken treatment for free XMe_3(X = N, P, and As) species are fairly coincident with the observed structural parameters in $[Co(acac)_2(Me_2XCH_2CH_2NH_2)]ClO_4$(X = N, P, and As) complexes. Either the observed or the calculated bond distances of X—C are well coincident with the sum of covalent radii of X and C atoms, and increases in the order X = N > P > As. Both of the crystallographic and theoretical bond angles C—X—C decreases in the order X = N > P > As. These tendencies, which are well-known in VSEPR consideration [12] demonstrate the decrease of the electronegativity of the X atom and the increase of the p(X atom) character on the X—C bonds. The increase on the p(X atom) character of the X—C bonds is more comfortable for the π interaction between $d\pi$(Co) orbitals and the π-type filled XMe_3 molecular orbitals with **e** symmetry (under C_{3v} assumption). The energies of the **e** orbitals of XMe_3 are −13.6 eV for X = N, −12.3 eV for X = P, and −10.5 eV for X = As. The order of the **e** orbital energies is N < P < As, which is similar to the order of the $E_{1/2}$(ox) values (N < P ⩽ As) as shown in Figs. 1(a), (b), and (c). Here, it should be but we could not consider the magnitude of the orbital overlapping. The calculated energies of the unoccupied **e*** orbitals which have an X—C antibonding character are +8.1 eV for X = N, +5.5 eV for X = P, and +11.6 eV for X = As. The Mulliken treatment suggests that the ability of π-back donation increases in the order: As < N < P. However, such a phenomenon of the π-back donation is not observed on the $E_{1/2}$(ox) values. Then we presume that the π-back donating interaction is negligible between the —XMe_2 groups and a Co^{III} ion.

Now we can demonstrate quantitatively that the electrochemical measurements for well-tailored complexes reveal the σ and π interactions between ligands and central metal atoms.

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Table 2. Selected bond distances (Å) and angles (°) of $[Co(acac)_2\{NH_2CH_2CH_2X(CH_3)_2\}]ClO_4$(X = N, P, and As) [1], and calculated optimal geometry and orbital energies by Mulliken for free $X(CH_3)_3$ species

	X = N [1]	Calc. for free NMe_3	X = P [1]	Calc. for free PMe_3	X = As	Calc. for free $AsMe_3$
X—Co (Å)	2.02		2.24		2.30	
X—C (Å)	1.53	1.45	1.82	1.85	1.93	1.93
X—C (Σr_{cov})[a] (Å)	1.52		1.87		1.99	
C—X—C (°)	109.5	111.9	108.3	100.0	106.2	97.2
Co—X—C (°)	109.8		110.6		112.4	
E(**a**)[b] (eV)		−9.4		−8.8		−6.9
E(**e**)[c] (eV)		−13.6		−12.3		−10.5
E(**e***)[d] (eV)		8.1		5.5		11.6

[a] The sum of covalent radii of X and C was obtained from Huheey, J. E., *Inorganic Chemistry*, 3rd ed., Harper and Row Publishers, Inc, 1983.

[b] E(**a**) denotes the energy of the occupied σ-type MO of XMe_3 with **a** symmetry (C_{3v}).

[c] E(**e**) denotes the energy of the occupied π-type MO of XMe_3 with **e** symmetry (C_{3v}).

[d] E(**e***) denotes the energy of the unoccupied π-type MO of XMe_3 with **e*** symmetry (C_{3v}).

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