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Ion Association of Caged Cobalt(III) Complexes in Aqueous Solution Governed by Double Hydrogen Bonding

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The pK_a values of four macrotricyclic hexaamine cage complexes of cobalt(III) have been measured to show that these complexes are 3–6 orders of magnitude more acidic than ordinary cobalt(III) amine complexes. The association constants K between the complexes and sulfate(2–) and malonate(2–) ions in aqueous solution have been determined. The log K values for both anions increase linearly as the pK_a values of the complexes decrease. This result, in conjunction with the circular dichroism changes due to the anions, indicates that the K values are dominated by the contribution from double hydrogen bonding between amine hydrogens of the complexes and two oxygen atoms of the anions.

Introduction

The importance of ion-pair formation in solution will be readily appreciated if we note that kinetic forms and steric courses of many reactions of metal complexes are affected by ion association. Very often, hydrogen-bonded structures were proposed for ion pairs.[1,2] It appears, however, that the problem, to what extent hydrogen bonding contributes to the stabilization of such ion pairs, especially in aqueous solution, is unsettled.[2]

The macrotricyclic hexaamine cage complexes of cobalt(III) synthesized recently by Sargeson and collaborators were reported[3] to show substantially higher acidities than ordinary $[Co(N)_6]^{3+}$ amine complexes, which usually have pK_a values greater than 14. Thus, these caged cobalt(III) complexes may be considered to have a greater tendency toward hydrogen bonding in aqueous solution and therefore to be suitable for evaluating the contribution of hydrogen bonding to the stabilization of ion pairs. In this work, we have determined the acidities of caged cobalt(III) complexes I–IV illustrated in Figure 1 and their association constants with sulfate(2–) and malonate(2–) ions. In light of the correlation found between the pK_a values and the association constants, the relative importance of various factors that may affect association constants in aqueous solution has been discussed.

Experimental Section

The perchlorate salts of III and IV were prepared by the literature methods.[3,4] Anal. Calcd for Δ-$[Co(sep)](ClO_4)_3 \cdot H_2O$: C, 21.78, N, 16.93; H, 4.87. Found: C, 21.82; N, 16.69; H, 4.88. Calcd for Δ-$[Co(azaMEsar)](ClO_4)_3 \cdot 3H_2O$: C, 23.66; N, 13.79; H, 5.53. Found: C, 23.83; N, 13.84; H, 5.26. The chloride salts of these complex ions were obtained by metathesis using potassium chloride.

The UV/vis and circular dichroism (CD) spectra were recorded at 25.0 °C on a Shimadzu UV-200 double-beam spectrophotometer and a Jasco J-40CS recording spectropolarimeter, respectively. The pK_a values were determined by following UV/vis and CD spectra of complex chlorides (2.5 mM) dissolved in 1 M KCl/NaOH solutions. The pH was measured by a Hitachi-Horiba Model F-7 pH meter at 20 °C.

Preparation of Δ-[Co(NOMesar)]$^{3+}$ (II). This complex was prepared by a method similar to that used for the preparation of $[Co(NO_2capten)]^{3+}$ (NO_2capten = 1-methyl-8-nitro-3,13,16-trithia-6,10,19-triazabicyclo[6.6.6]eicosane).[5] To a stirred aqueous solution (300 mL) of Na_2CO_3 (6.0 g) and Δ-$[Co(sen)]Cl_3$ (4.1 g, 8.1 mM) (se = 1,1,1-tris(4-amino-2-azabutyl)ethane)[6] were added nitromethane (5.0 g, 80 mM) and 36% aqueous formaldehyde (50 g, 0.58 M). After stirring for 2 h, the solution was filtered and the filtrate acidified with acetic acid to about pH 4, diluted with water (1 L), and sorbed on an ion-exchange column of SP Sephadex C-25 (Na^+ form). The column was washed with 1 L of water, and the complex was eluted with 0.2 M solution of sodium chloride. The eluate was concentrated on a rotatory evaporator to give orange crystals, which were then washed with a small quantity of water and ethanol. Anal. Calcd for Δ-$[Co(NOMEsar)]Cl_3 \cdot 5H_2O$: C, 30.39; N, 16.54; H, 6.30. Found: C, 30.54; N, 16.59; H, 6.14. The perchlorate salt was obtained by adding a concentrated aqueous solution of sodium perchlorate to an aqueous solution of the chloride. Anal. Calcd for Δ-$[Co(NOMEsar)](ClO_4)_3$: C, 25.71; N, 13.99; H, 4.75. Found: C, 25.95; N, 14.28; H, 5.04.

Preparation of Δ-[Co(diNOsar)]$^{3+}$ (I). This complex was prepared by a method similar to that described above for II. An essentially similar method was reported recently.[7] The choice of the counteranion (X) of the starting material Δ-$[Co(en)_3]X_3$ (en = ethylenediamine) appeared to be crucial, because the iodide and perchlorate salts caused precipitation of partly reacted complexes. The yield was about 76%, based on the starting material with X = Cl^- or NO_3^-. Anal. Calcd for Δ-$[Co(diNOsar)]Cl_3 \cdot 0.5NaCl \cdot 0.5H_2O$: C, 29.09; N, 19.39; H, 5.41. Found: C, 28.96; N, 19.34; H, 5.61. The perchlorate salt was obtained similarly as for II. Anal. Calcd for Δ-$[Co(diNOsar)](ClO_4)_3 \cdot 2H_2O$: C, 21.89; N, 14.60; H, 4.43. Found: C, 21.96; N, 14.60; H, 4.25.

We noticed that the perchlorate salts of I and II decompose thermally in the solid state and in the dark, over a period of months. This solid-state reaction can be confirmed most conveniently by CD. This aspect will be published separately.

Association Constants. The association constant, K, for the equilibrium

$$M^{3+} + A^{2-} \rightleftharpoons [MA]^+ \qquad (1)$$

was obtained by a method described in previous studies.[1a,b] Briefly, it involves the least-squares fitting to the equation

$$c_M/DCD = 1/K(c_A - x)(\Delta\epsilon_{MA} - \Delta\epsilon_M) + 1/(\Delta\epsilon_{MA} - \Delta\epsilon_M) \qquad (2)$$

where c_M and c_A are the initial concentrations of M^{3+} and A^{2-}, respectively, x is the concentration of $[MA]^+$, and $\Delta\epsilon_{MA}$ and $\Delta\epsilon_M$ refer to the molar $\Delta\epsilon$ values of $[MA]^+$ and M^{3+}, respectively. DCD is defined as the CD intensity with A^{2-} minus the CD intensity without A^{2-}. The metl

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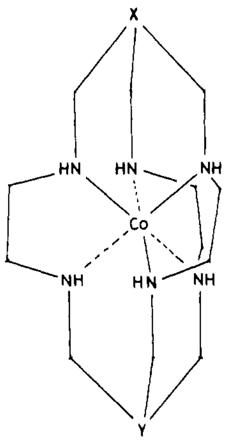

	X	Y
I	CNO_2	CNO_2
II	CCH_3	CNO_2
III	N	N
IV	N	CCH_3

Figure 1. Structures of the Δ complexes examined in this work: I, Δ-[Co(diNOsar)]$^{3+}$: II, Δ-[Co(NOMEsar)]$^{3+}$: III, Δ-[Co(sep)]$^{3+}$: IV, Δ-[Co(azaMEsar)]$^{3+}$. Key: diNOsar = 3,6,10,13,16,19-hexaaza-1,8-dinitrobicyclo[6.6.6]eicosane; NOMEsar = 3,6,10,13,16,19-hexaaza-1-methyl-8-nitrobicyclo[6.6.6]eicosane; sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane; azaMEsar = 1,3,6,10,13,16,19-heptaaza-8-methylbicyclo[6.6.6]eicosane.

Table I. Association Constants of the Δ Complexes at 25.0 °C and $\mu = 0.1$ ($NaClO_4$)

complex	SO_4^{2-}			$CH_2(COO)_2^{2-}$		
	λ, nm	K, M^{-1}	$\Delta\epsilon_{MA}$	λ, nm	K, M^{-1}	$\Delta\epsilon_{MA}$
I	365	269 ± 48	0.41	355	232 ± 33	0.59
	360	289 ± 56	0.41	360	247 ± 12	0.57
II	365	209 ± 93	0.15	365	131 ± 17	0.19
				365	137 ± 13	0.18
III	510	94 ± 2	−0.12	430	85 ± 8	0.70
				500	80 ± 2	−0.01
IV	435	57 ± 7	0.76	424	62 ± 3	0.64
				500	59 ± 5	0.52

concentration, c_M, was set to 3.0×10^{-4} M for all systems and c_A was changed from 0 to 2.73×10^{-2} M for III and IV. At higher metal concentrations, rather insoluble $[M]ClO_4{\cdot}SO_4$ and $[M]ClO_4{\cdot}CH_2(COO)_2$ species precipitated. Ionic strength was adjusted to $\mu = 0.1$ with sodium perchlorate.

Since the complexes I and II were found to associate with perchlorate ions added as the swamping electrolyte, the following procedure was used to determine the association constants with malonate and sulfate. First, the thermodynamic association constant, K^0, between I and ClO_4^- was estimated by following CD changes due to successive addition of $NaClO_4$ (up to 0.2 M) and analyzing the DCD data by the Nyman and Plane's procedure.[8] From K^0, the corresponding concentration quotient, $K(ClO_4^-)$, at $\mu = 0.1$ was calculated by eq 2 of ref 8, where $c = 0.3$ was used.[9] The value $K(ClO_4^-) = 0.54$ M^{-1} ($\mu = 0.1$) derived in this way implied that if c_A, and hence the concentration of ClO_4^-, is the same as that used for III and IV, the proportion of I associated with ClO_4^- changes from one sample solution to another. Thus, to obtain the association constants with malonate and sulfate, c_M and c_A were limited to be very small ($c_M = 3.0 \times 10^{-4}$ M and $c_A = 0–3.33 \times 10^{-3}$ M). At this combination of concentrations, the percentage of I associated with ClO_4^- was estimated to be very small and almost constant (4.55–4.96%). Thus, in the analysis of DCD data by eq 2 for malonate and sulfate, c_M in eq 2 was set equal to 95% of the total complex concentration. In actuality, however, this correction did not affect the resulting K value, which will be evident from the form of eq 2 if we note that K is obtained as the (intercept)/(slope) ratio and this ratio is not affected by c_M. Also, the low c_M and c_A values assure that the ionic strength changes that would be brought about by an appreciable association with malonate or sulfate (see Table I) can safely be neglected. The DCD data were collected for wavelengths at which the CD intensity of I was not affected by ClO_4^-.

For II, $K(ClO_4^-)$ was not obtained owing to very small CD changes due to ClO_4^-. The association constant between II and malonate or sulfate was determined from the same wavelength and concentrations as for I. However, the K value of II with sulfate could not be determined accurately because of the absence of suitable wavelength, i.e., a wavelength at which the CD intensity of II is not affected by ClO_4^- yet affected measurably by sulfate. This caused an especially larger error in K for this system (see Table I).

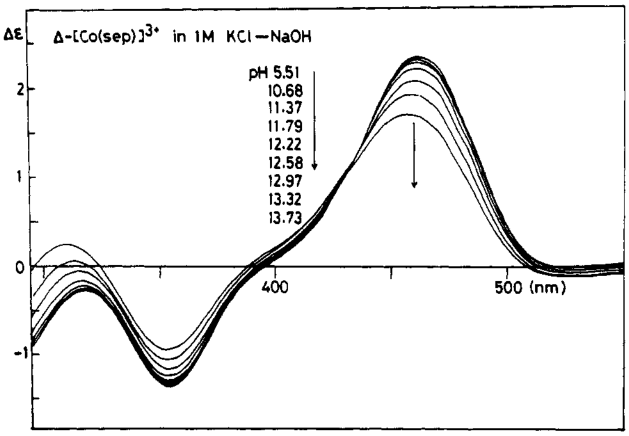

Figure 2. CD spectra of III at several pH values. Both pH and CD change successively in the order indicated by arrows.

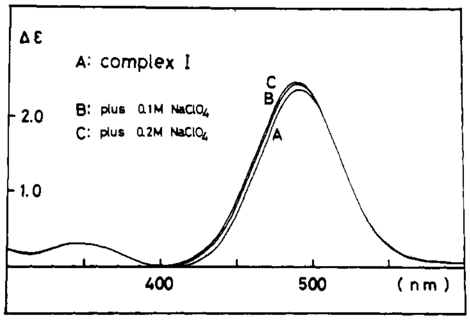

Figure 3. CD spectra of I in the absence (A) and presence (B, C) of sodium perchlorate.

Results and Discussion

Acidity. All the complexes exhibited a similar color change from orange to intense purple at higher pH values. The same color change was reported[10] for III in organic solvents and attributed to deprotonation. The acidity of NH hydrogens of the complexes I–IV has been measured in 1 M KCl/NaOH solutions, by following the CD and UV/vis spectral changes. In Figure 2, the CD spectra of III taken at several pH values are given. The spectra at lower pH values formed a well-defined isodichroic point at about 437 nm, but at higher pH values the isodichroic point was obscured by a CD change due to ion pairing with OH^- ions. The complex IV showed a similar spectral change. Since the spectrum corresponding to the fully deprotonated species could not be obtained for both III and IV at pH <14, the pK_a values of these ions could not be determined accurately. For the same reason, the pK_{a2} value corresponding to the second ionization of I and II could not be obtained with certainty. The pK_a values estimated are 12.6 for III, 13.2 for IV, 10.9 and 13.5 for II,[3b,c] and 10.0 and 11.5 for I. The effect of X and Y substituents of Figure 1 upon the pK_a values is evident, and the acidity variation may be understood by noting that the electron-withdrawing effect decreases in the order $C–NO_2 > N > C–CH_3$. The pK_a values obtained here may be contrasted with the pK_a value of 15.9 estimated[11] for the parent $[Co(en)_3]^{3+}$ ion. Thus, the present complexes are 3–6 pH units more acidic than ordinary $[Co(N)_6]^{3+}$ amine complexes. This decrease in pK_a might be attributed to a combined action of the inductive effect of capping groups and the change of coordinated nitrogens from primary to secondary. A similar decrease in pK_a has also been observed for the plati-

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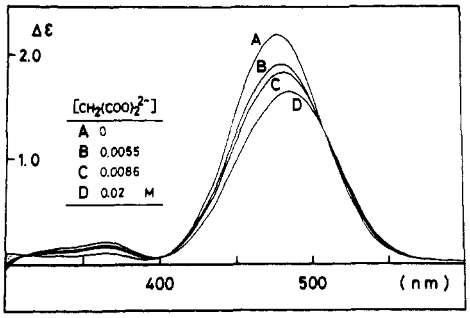

Figure 4. Spectral change of II due to successive addition of malonate (μ = 0.1 with $NaClO_4$).

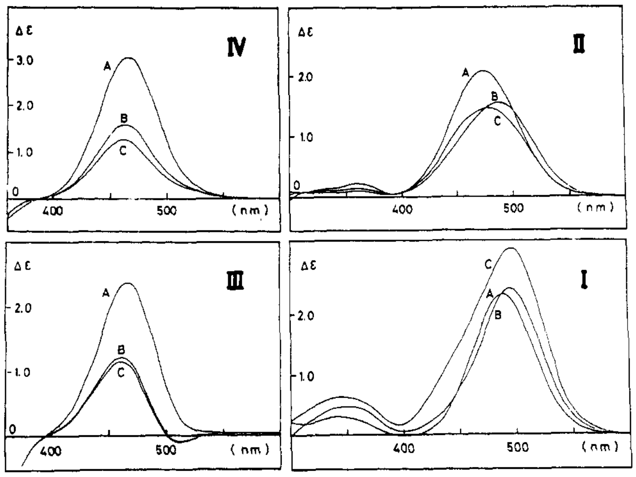

Figure 5. CD spectra of free complex (A) and of ion pairs with malonate (B) and sulfate (C).

num(IV) analogues of I and III.[12]

Association with Perchlorate Ion. Evidence has been obtained for the association of ClO_4^- with complex I. Since sodium perchlorate has been used widely as the swamping electrolyte to adjust ionic strength,[1,2] this may warrant some comments. Addition of sodium perchlorate had no effect on the CD spectra of III and IV. The CD spectrum of I changed appreciably by sodium perchlorate, contrary to a common observation that the perchlorate ion does not affect UV/vis and CD spectra for most complexes.[13] Figure 3 shows the CD spectra of I taken in the absence and presence of sodium perchlorate. The spectral change was large enough to allow us to determine the association constant with ClO_4^-, $K(ClO_4^-)$. We estimated $K(ClO_4^-) = 0.54\ M^{-1}$ at $\mu = 0.1$. To our knowledge, the association constant with perchlorate ion in aqueous solution has not been determined directly by use of spectral changes, even for higher charged complexes like $[Pt(en)_3]^{4+}$.[8,13]

The systems involving II provided another interesting feature. Figure 4 illustrates the spectral change of II due to succesive addition of malonate. It can be seen that all the spectra form isodichroic points at about 400 and 505 nm. Usually, such a spectral change has been taken as evidence for 1:1 association, or equally for the absence of both interference by ClO_4^- and 1:2 association. The CD spectrum of II changed, however, by the addition of $NaClO_4$, and this spectral change was very similar to that given in Figure 3, though the magnitude of the CD change was much smaller. Since the perchlorate ion did not affect the spectrum of II outside the region 400 nm < λ < 500 nm (see Figure 3), the isodichroic points observed in Figure 4 are real ones. Further, the 1/DCD vs. $1/(c_A - x)$ plots of eq 2 were linear. These observations illustrate a dangerous aspect of the common practice that the linearity of eq 2 and the formation of isosbestic point(s) are the enough condition for 1:1 association.

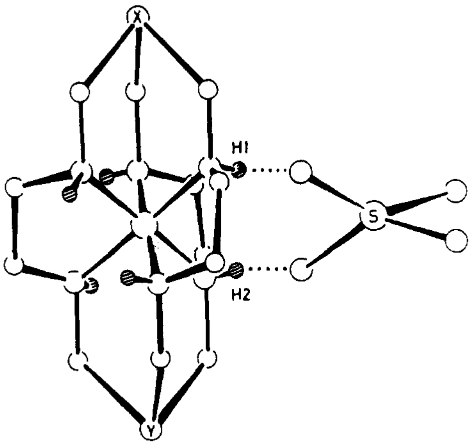

Figure 6. Proposed mode of association with sulfate.

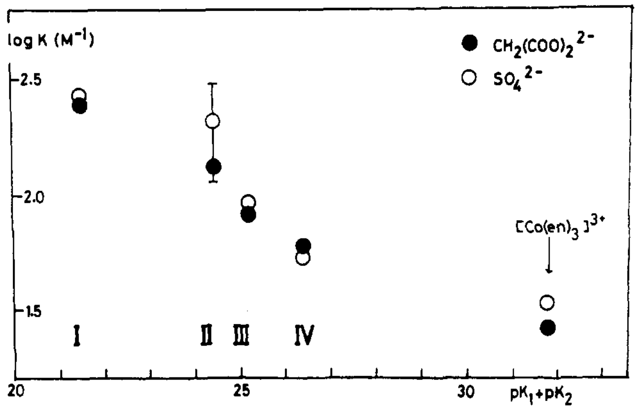

Figure 7. log K vs. pK_a plots. For the large error in the association constant between II and SO_4^{2-}, see text.

Association Constant. The determination of association constants with malonate and sulfate was performed by taking the above precautions. The results are listed in Table I, together with the Δε values of ion-paired species. Figure 5 summarizes the CD spectra of free metal ions (A) and the CD spectra of ion pairs with malonate (B) and sulfate (C). Except for the case of I, all the CD changes due to ion pairing are in such a direction that they enhance the E_a rotational strengths. This type of CD change has been taken,[1a,b,e,2a] for complexes with D_3 symmetry, to indicate the association of an anion along the D_3 equatorial direction. This inference coincides exactly with the deduction from structural features of the complexes; the complexes possess NH hydrogens that are directed only in the D_3 equatorial direction. The association along the C_2 (equatorial) direction appears to be the only possibility in view of the presence of large capping groups. Further, the NH hydrogens are disposed very nicely[1a,b,4] for double hydrogen bonding with two oxygen atoms of both sulfate and malonate ions. In fact, such hydrogen bonding has been found in the crystal of $[Co(sep)]S_2O_6{\cdot}H_2O$.[3] Therefore, the mode of association would be as depicted in Figure 6.

Figure 7 plots log K values against pK_a. The abscissa is either pK_{a1} + pK_{a2} in cases where both values are available as in I and II or 2pK_a for III, IV, and $[Co(en)_3]^{3+}$. For comparison, the data[11,14] of $[Co(en)_3]^{3+}$ are also plotted. It is evident from Figure 7 that the K values of the present complexes are much larger than those of $[Co(en)_3]^{3+}$. In fact, reported values of association constants between cobalt(III) hexaamine type complexes and dinegative anions come up at most to about 70 M^{-1} at μ = 0.1

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[15] See, e.g.: Pipkin, J. D.; Stella, V. J. *J. Am. Chem. Soc.* **1982**, *104*, 6672–6680.

and 25 °C, and a value exceeding 100 M^{-1} does not seem to be reported so far. Further, the association constants obtained for I–IV increase as the acidity of the complexes increases, and a good linear correlation between log *K* and pK_a may be observed in Figure 7. A linear regression analysis for the malonate and sulfate systems yields 0.98 and 0.90 as the correlation coefficients, but these figures should not be taken too literally because of rather large uncertainties in pK_a values and some *K* values. Thus, log *K* can also be correlated with pK_{a1} alone rather well. Even with these reservations, the correlation seems satisfactory. With the CD changes in Figure 5 and the correlation in Figure 7 taken together, it appears reasonable to conclude that the malonate and sulfate anions approach the complex cations from the D_3 equatorial direction and hydrogen bond, via two oxygen atoms of the anions, to two NH hydrogens of the cations, and the stability of the ion pairs is governed by this double hydrogen bonding.

It seems pertinent to consider here the factors that may affect the value of the outer-sphere association constant in aqueous solution. Here, we will confine our discussion to such complexes that do not contain very hydrophobic ligands, as typified by 1,10-phenanthroline or 2,2′-bipyridine. For complexes with an overall charge of 1+ or 2+, we have pointed out that the dominant factor is the size of the interacting ions; as the ions get larger[16] and hence assume more and more the character of water-structure breaker,[17] the association constant increases. Here, it was noted that it is the crystallographic volume, not the hydrodynamic volume, of the ions that governs the association constant. This appears to be suggestive of contact ion pairs. For complexes with an overall charge of 3+, it is certain that interionic electrostatic force usually contributes significantly. This will be readily appreciated if we note a general trend in association constant that tripositive complex cations exhibit much larger association constant for most simple anions like Cl^-, Br^-, NO_3^-, SO_4^{2-}, or $S_2O_3^{2-}$ than monopositive and dipositive complex cations.[2c] However, a cursory examination of previous results reveals immediately that the electrostatic force alone may not explain the variation of *K* values. For example, the *K* values of $[Co(en)_3]^{3+}$ for *o*- and *p*-phthalate dianions are repoted to be about 65 and 2.8 M^{-1}, respectively, at $\mu = 0.1$ ($NaClO_4$) and 25 °C.[1j] Likewise, large differences in *K* values of perhaps a similar nature can also be found for $[Co(en)_3]^{3+}\cdots$maleate/fumarate and $[Co(en)_3]^{3+}\cdots$*cis*-1,2-/1,4-cyclohexanedicarboxylates (48 vs. 3.5 M^{-1} and 70 vs. 8.5 M^{-1}, respectively, under the same condition as above),[1j,14] despite the same 3+/2− combination. Since such large differences in *K* values may not be accommodated by a simple electrostatic consideration[18] and only those anions that can allow both carboxyl groups to take part in bonding to NH hydrogens of the cation simultaneously exhibited large *K* values, the importance of hydrogen bonding has been stressed.[14] Therefore, it may be inferred that both electrostatic force and hydrogen bonding contribute significantly for tripositive complexes. The relative importance of the two effects has not always been assessed. We believe that the present result provides an unequivocal example where ion pairing is controlled by (double) hydrogen bonding.

The results presented in Figure 7 might appear at first sight to suggest that the *K* values of ordinary complexes with $pK_a >$ 14 are dominated by factors other than hydrogen bonding; hydrogen bonding plays a minor role in $[Co(en)_3]^{3+}$. Though double hydrogen bonding with $[Co(en)_3]^{3+}$ as depicted in Figure 6 is equally plausible structurally as for the present complexes, a completely different mode of association has been proposed for $[Co(en)_3]^{3+}$.[1c,d,2a] In the ion pair $[Co(en)_3]^{3+}\cdots SO_4^{2-}$, for example, the sulfate ion has been assumed to approach the cation along the cation's C_3 axis and hydrogen bond, through three oxygen atoms, to three NH hydrogens of the cation that are oriented in the C_3 direction. For the dicarboxylate anions cited above, a similar C_3 access has been postulated. Therefore, it may be inappropriate to discuss $[Co(en)_3]^{3+}$ and the present complexes on the same basis.

From Figure 7 and Table I, it is seen that the association constant with malonate is rather similar to that with sulfate for all the complexes investigated in this work. This similarity in *K* values is puzzling for the present systems, where the dominant factor in *K* is most probably the hydrogen bonding; in hydrogen-bonded systems, the *K* values are expected to depend not only on the acidity of the complexes but also on the basicity of the anion.[15] This reasoning leads us to expect that the sulfate ion should have smaller *K* values than the malonate ion, because the former is less basic than the latter. Though the difference in *K* values is not large, especially for IV, the results in Table I do not appear to support this expectation. In this contrast, it may be worhwhile to point out that such an expectation is not fulfilled also for systems like $[Co(en)_3]^{3+}\cdots$dicarboxylate dianions, where hydrogen bonding is considered to be the dominant contributor.

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Molecular Orbital Justification of Topological Electron-Counting Theory

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It is shown that the rules for determining the parameter *X* of the topological electron-counting (TEC) theory or its generalized version can be justified within the framework of molecular orbital theory. The parameter *X* can be interpreted as the number of "missing" antibonding cluster orbitals, or more precisely $X = E - A$, where *E* is the number of edges and *A* is the number of antibonding cluster orbitals. It is also shown that the number of *bonding* cluster orbitals corresponds to the number of skeletal electron pairs in the context of the widely used skeletal electron pair (SEP) theory. Consequently, both rules can be derived from molecular orbital calculations and vice versa. Qualitative correlation and interaction diagrams are constructed for the conversion of prisms to antiprisms, pyramids to bipyramids, and prisms to bicapped prisms. Multiple *X* values, and hence multiple electron counts, for certain polyhedral clusters are also justified and illustrated with examples.

Introduction

Recently we developed a new topological electron-counting (TEC) theory for polyhedral metal clusters based on Euler's theorem and the effective atomic number (EAN) rule for transition metals.[1] This theory was subsequently generalized to include polyhedral clusters containing both main-group and transition-metal elements.[2] This simple electron-counting rule can be used

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