Short Communication

Effect of Protonation on the Electronic Spectra of Some Cobalt(III) Cage Complexes

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The spectra of Co(III) cage complexes of the type $[Co(H_3CsarNHR)]^{3+/4+}$ (sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane) with R = –H, $-CH_2CH_2NH_3^+$ or $-CH_2(4\text{-}pyH^+)$ (py=pyridine) (Fig. 1) display significant variations with the hydrogen ion concentration in the 0.001–3.0 M region. Thus, the second d–d band, which is otherwise obscured by charge-transfer bands, appears as a distinct band in a strong acidic medium.[1] For R = –H the changes were small (Fig. 2), but with the other substituents the effect was larger (Fig. 3). The effect seemed to be correlated with protonation on the apical amine group (ca. 4.5 Å from the metal centre), and (except for R = –H) the $[H^+]$ range indicated very low pK_a values. These spectral changes allow an estimate of these very low pK_a values, which are otherwise difficult to obtain.

Experimental

All Co(III) cage complexes were prepared as described elsewhere.[1–4] For the compounds $[Co(H_3CsarNH_3)]Cl_4\cdot ½H_2O$,[2] $[Co(H_3CsarNH_2CH_2CH_2NH_3)]Cl_5\cdot H_2O$[3] and $[Co(H_3CsarNHCH_2py)]\ (O_3SCF_3)_3\cdot H_2O$,[1] solutions with varying $[H^+]$ but with constant complex concentrations ($\approx 3\times10^{-3}$ M) were made from stock solutions of the complex, $HClO_4$ or NaOH, and $NaClO_4$. The ionic strength was kept constant for each series of measurements [$\mu = 1.0$ or 6.0 M $(H/Na)ClO_4$]. Visible absorption spectra were recorded on a Perkin-Elmer Lambda 2 spectrophotometer connected to a PC. A Radiometer PHM 82 pH-meter with a G 202 C glass electrode and a K 401 calomel electrode was used to measure $[H^+]$ of the solutions (in the 1.0 M series). A calibration curve was made from solutions [μ = 1.0 M $(H/Na)ClO_4$] with $[H^+]$ in the range 1×10^{-4}–1.0 M. The absorption data and the $[H^+]$ data were used to calculate pK_a values. Acid concentration dissociation constants at 25.0 °C and μ = 1.00 M $(NaClO_4)$ were also determined by regression analysis of titration data as described by Mønsted and Mønsted.[5] In case of strong acids, titration did not give much information and the pK_a value could only be estimated to be less than 2.

The Co(III) cage complexes, $[Co(H_3NsarNH_3)]Cl_5$,[2] $[Co(H_3CsarNH_2CH_2CH_2NH_2pyH)]Cl_6$,[1] $[Co(H_3CsarNH_2CH_2COOH)]Cl_5$,[4] $[Co(ClsarCl)]Cl_3$[2] and $[Co(H_3CsarNO_2)]Cl_3$,[2] were also examined.

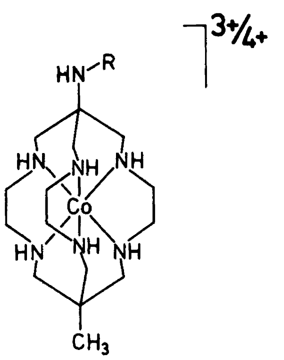

Fig. 1. Drawing of the Co(III) cage complex ion $[Co(H_3CsarNHR)]^{3+/4+}$.

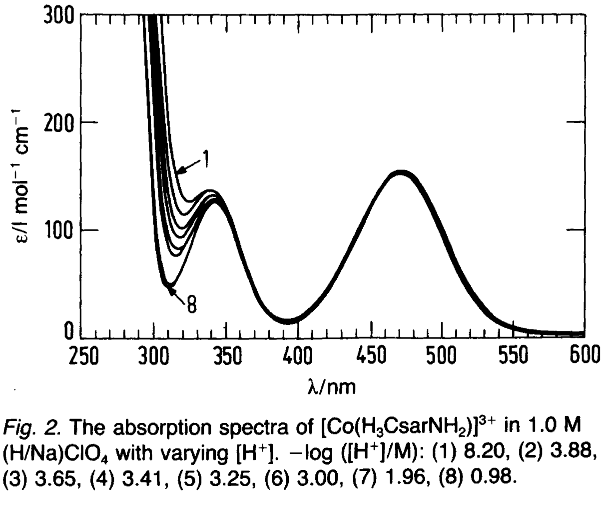

Fig. 2. The absorption spectra of $[Co(H_3CsarNH_2)]^{3+}$ in 1.0 M $(H/Na)ClO_4$ with varying $[H^+]$. $-\log([H^+]/M)$: (1) 8.20, (2) 3.88, (3) 3.65, (4) 3.41, (5) 3.25, (6) 3.00, (7) 1.96, (8) 0.98.

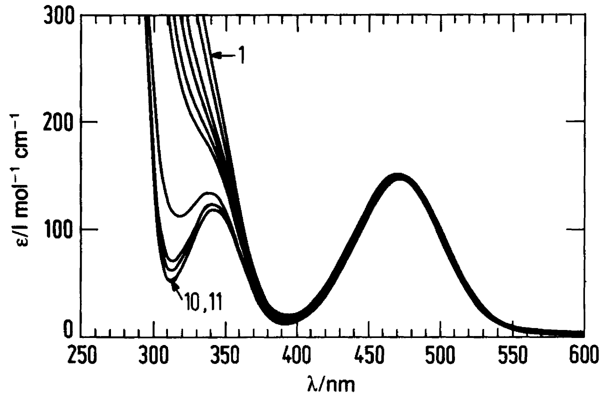

Fig. 3. The absorption spectra of $[Co(H_3CsarNHCH_2CH_2NH_3)]^{4+}$ [1–6 in 1.0 M $(H/Na)ClO_4$, 7–11 in 6.0 M $(H/Na)ClO_4$] with varying $[H^+]$. $-\log$ $([H^+]/M)$: (1) 2.71, (2) 0.98, (3) 0.58, (4) 0.38, (5) 0.27, (6) 0.25, (7) −0.22, (8) −0.26, (9) −0.48, (10) −0.62, (11) −0.73.

Table 1. Acid dissociation [25 °C, μ = 1.00 M $(NaClO_4)$] constants.

Complex	pK^a	pK^b
$[Co(H_3CsarNH_3)]^{4+}$	3.5(1)	3.43(1)
$[Co(H_3CsarNH_2CH_2CH_2NH_3)]^{5+}$	0.3	≈ 1^c
$[Co(H_3CsarNH_2CH_2pyH)]^{5+}$	0	< 2^c

^{a}Calculated from spectral changes. ^{b}Determined by potentiometric methods. ^{c}Ref. 1.

Results and discussion

The spectra of $[Co(H_3CsarNH_3)]^{4+}$, $[Co(H_3CsarNH_2CH_2CH_2NH_3)]^{5+}$, $[Co(H_3CsarNH_2CH_2pyH)]^{5+}$, $[Co(H_3NsarNH_3)]^{5+}$, $[Co(H_3CsarNH_2CH_2CH_2NH_2CH_2pyH)]^{6+}$ and $[Co(H_3CsarNH_2CH_2COOH)]^{4+}$ showed a significant dependence on $[H^+]$ in the 10^{-5}–1 M region, whereas the spectra of $[Co(ClsarCl)]^{3+}$ and $[Co(H_3CsarNO_2)]^{3+}$ did not display such changes. These spectral changes in the 300–400 nm region brought about by changing $[H^+]$ (Figs. 2 and 3) can be correlated with an equilibrium between a protonated and an unprotonated species. The most likely site of protonation is the non-coordinated apical amine groups of these complexes. Protonation at one of the coordinated amine groups and decomplexation seems unlikely, as the position and shape of the d–d bands was unchanged and since no effect was seen for $[Co(ClsarCl)]^{3+}$ or $[Co(H_3CsarNO_2)]^{3+}$. The pK_a values were calculated at two different wavelengths and compared with values found by potentiometric titration (Table 1) of the same systems. The agreement was good, especially for $[Co(H_3CsarNH_3)]^{4+}$. For $[Co(H_3CsarNH_2CH_2CH_2NH_3)]^{5+}$ and for $[Co(H_3CsarNH_2CH_2pyH)]^{5+}$ it was necessary to use 3.0 M $HClO_4$ [μ = 6.0 M $(H/Na)ClO_4$] to obtain the fully protonated complex, and values for the molar absorptivity of the acid form obtained in this way were used in the calculations on the data from the 1.0 M series.

The very strong acidity of $[Co(H_3CsarNH_2CH_2CH_2NH_3)]^{5+}$ (pK_a ≈ 0) and $[Co(H_3CsarNH_2CH_2pyH)]^{5+}$ (pK_a = 0.3) relative to $[Co(H_3CsarNH_3)]^{4+}$ (pK_a = 3.5) is probably due both to a substitution effect[1] and to the additional charge of the complex. Similar changes in the spectral properties were reported by Ogino[6] for for the non-cage complex $[(H_3N)_5Co(NH_2CH_2CH_2NH_3)]^{4+}$ (pK_a = 7.5) and were correlated with protonation at the pendant amine of the monodentate 1,2-ethanediamine ligand. An explanation involving an intramolecular interaction between the pendant amine and one of the coordinated ammonia ligands was proposed.[6] The Co(III) cage complexes are quite rigid, with a relatively long distance (≈ 3.7 Å) between the apical N and one of the nearest coordinated nitrogen atoms compared to the distance (≈ 2.7 Å) found between two coordinated nitrogen atoms also connected by a –C–C– bridge. Intramolecular hydrogen bonding between the apical amine and one of the coordinated amines seems unlikely in view of the distance and rigidity of the cage. Therefore these complexes call for a different explanation. A possible simple interpretation is that for electrostatic reasons it would require more energy to transfer positive charge from the cobalt centre to the positively charged protonated ligand than to a neutral unprotonated ligand.

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