OUTER-SPHERE CHARGE-TRANSFER EXCITATION IN THE ION PAIR $[Co(NH_3)_6]^{3+}[B_{12}H_{12}]^{2-}$

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Received June 5, 2000
Accepted August 31, 2000

In commemoration of Professor Antonín A. Vlček.

The aqueous ion pair $[Co(NH_3)_6]^{3+}[B_{12}H_{12}]^{2-}$ displays an UV absorption at λ_{max} = 250 nm which is assigned to an outer-sphere charge-transfer (OSCT) transition from $[B_{12}H_{12}]^{2-}$ to $[Co(NH_3)_6]^{3+}$. OSCT excitation leads to photoredox reaction with the formation of Co^{2+} (Φ = 0.03 at λ_{irr} = 313 nm).

Keywords: Charge transfer complexes; Photochemistry; Cobalt(III) complexes; Boranates; Boranes; UV spectroscopy.

Electron transfer processes play a fundamental role in coordination chemistry. Our current knowledge is largely based on electrochemical studies. This subject was pioneered by A. A. Vlček who recently presented as his legacy an overview on the achievements and new trends in molecular electrochemistry of coordination compounds[1]. Vlček's earlier investigations included the examination of redox properties of $[Co(NH_3)_6]^{3+}$ (refs[2,3]). This cation can not only be reduced electrochemically but also photochemically. In this context it is of interest that ion pairs of the type $[Co(NH_3)_6]^{3+}$ X^{n-} are well suited for examination of electron donor properties of reducing anions X^{n-}, since they are characterized by outer-sphere charge transfer (OSCT) transitions that involve the promotion of electron from X^{n-} to $[Co(NH_3)_6]^{3+}$ (refs[4,5]). In a more general sense, X^{n-} as a constituent of such ion pairs can be also viewed as a ligand (second-sphere ligand) which may be redox active, too. The importance of ligand-based redox processes has been emphasized by A. A. Vlček some 20 years ago[6].

Boranes as ligands in transition metal complexes have attracted much attention[7–11]. Since boranes are generally reducing, such ligands are expected to participate in photochemical CT processes. Unfortunately,

doi: 10.1135/cccc20010119

metalloboranes possess complex molecular and electronic structures, hampering the investigation of their electronic spectra and photoreactivity. In a simple approach to this problem, we decided to study the ion pair $[Co(NH_3)_6]^{3+}[B_{12}H_{12}]^{2-}$.

BH_4^- as the parent of all hydridoborates is a versatile reducing agent, functioning as a hydride donor. Unfortunately, previous attempts to use BH_4^- as CT donor in ion pairs have failed[12]. This seems to be rather surprising in view of the well known OSCT absorptions of ion pairs such as $[Co(NH_3)_6]^{3+}BPh_4^-$ (refs[4,5,13]). However, BH_4^- is very reactive and undergoes a facile hydrolysis in the presence of water. On the contrary, $B_{12}H_{12}^{2-}$ (refs[14,15]) is completely stable in water. It belongs to a class of cluster anions with the general composition $B_nH_n^{2-}$ (refs[11,16]). These polyhedral closo-boranes possess remarkable properties. These very stable clusters have highly symmetrical structures and are regarded as three-dimensional aromatic species[17]. Moreover, calculations on the icosahedral $B_{12}H_{12}^{2-}$ have led to the conclusion that the extra charge of –2 is mainly localized on the surface of this dianion[18]. This should facilitate an OSCT interaction in the ion pair $[Co(NH_3)_6]^{3+}[B_{12}H_{12}]^{2-}$.

EXPERIMENTAL

Materials

$[Co(NH_3)_6]Cl_3$ and $K_2[B_{12}H_{12}]$ were obtained from Aldrich. The water used was triply destilled.

Apparatus

Absorption spectra were measured with Hewlett–Packard 8452A diode array or Uvikon 860 spectrophotometers. The light source used was an Osram HBO 100 W/2 or a Hanovia Xe/Hg 977 B-1 (1 kW) lamp. Monochromatic light was obtained using a Schoeffel GM 250/1 high-intensity monochromator (band width 23 nm). The photolyses were carried out in aqueous solutions in 1 cm cuvettes at room temperature. Progression of the photolyses was monitored by UV-VIS spectroscopy. For quantum yield determinations the complex concentrations were such as to achieve essentially complete light absorption. The total extent of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. Absorbed light intensities were determined by a Polytec pyroelectric radiometer that was calibrated by actinometry and equipped with a RkP-345 detector.

RESULTS

Upon mixing up aqueous solutions of $[Co(NH_3)_6]Cl_3$ and $K_2[B_{12}H_{12}]$, a new absorption appears that leads to increased absorbance in the UV spectral region (Fig. 1). The absorbance difference spectrum clearly reveals the existence of a new maximum. At fairly high equimolar concentrations ($2 \cdot 10^{-3}$ mol l^{-1}) of both ions, this band follows the Lambert–Beer law. It is assumed that at this concentration, ion pairing is complete. The new absorption at $\lambda_{max} = 250$ nm ($\varepsilon = 91$ mol^{-1} l cm^{-1}) has a half-width of $\Delta\bar{\nu}_{1/2} = 6\,800$ cm^{-1}. Deviation from the Lambert–Beer law at much lower concentrations ($<5 \cdot 10^{-4}$ mol l^{-1}) is used to estimate the ion pair association constant. The ion pair $[Co(NH_3)_6]^{3+}[B_{12}H_{12}]^{2-}$ is not very stable ($K = 290$ l mol^{-1}).

Upon irradiation of the aqueous ion pair $[Co(NH_3)_6]^{3+}[B_{12}H_{12}]^{2-}$ at λ_{irr} = 313 nm a photoredox reaction takes place. Reduced Co^{2+} determined spectrophotometrically as $[Co(NCS)_4]^{2-}$ ($\lambda_{max} = 625$ nm, $\varepsilon = 1\,700$ mol^{-1} l cm^{-1})[19] is formed with the quantum yield $\Phi = 0.03$ at $\lambda_{irr} = 313$ nm. The parent ion $[Co(NH_3)_6]^{3+}$ itself is hardly light-sensitive under these conditions. At λ_{irr} = 313 nm, Co^{2+} is formed with $\Phi < 10^{-3}$.

DISCUSSION

The complex $[Co(NH_3)_6]^{3+}$ shows two ligand field absorptions at $\lambda_{max} = 340$ nm ($\varepsilon = 46$ mol^{-1} l cm^{-1}) and 475 nm ($\varepsilon = 56$ mol^{-1} l cm^{-1}) and a more intense shorter-wavelength band which belongs to a ligand-to-metal charge transfer transition[20]. The anion $[B_{12}H_{12}]^{2-}$ starts to absorb at approximately 220 nm. The absorption maximum is located at $\lambda < 185$ nm (refs[15,21]). In analogy to various other ion pairs that consist of $[Co(NH_3)_6]^{3+}$ and a reduc-

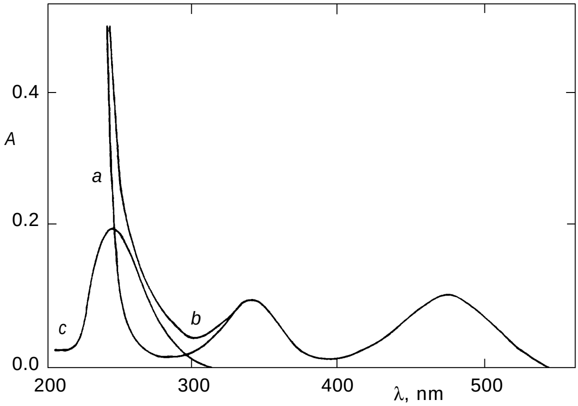

FIG. 1
Electronic absorption spectra of aqueous $4.08 \cdot 10^{-3}$ M $[Co(NH_3)_6]Cl_3$ and $4.08 \cdot 10^{-3}$ M $K_2[B_{12}H_{12}]$ recorded at room temperature in a 1 cm tandem cell: *a* separate solutions, *b* their mixture, *c* absorbance difference spectrum (*c* = *a* – *b*)

ing anion[4,5], the ion pair $[Co(NH_3)_6]^{3+}[B_{12}H_{12}]^{2-}$ shows a new absorption at λ_{max} = 250 nm (Fig. 1). It is attributed to an OSCT transition from $[B_{12}H_{12}]^{2-}$ to $[Co(NH_3)_6]^{3+}$. The intensity of this band (ε = 91 mol^{-1} l cm^{-1}) is comparable with that of the other ion pairs of this type. The assignment of this absorption is consistent with the photochemical behavior of the ion pair. Upon OSCT excitation, $[Co(NH_3)_6]^{3+}$ is reduced to Co^{2+}. Since $[B_{24}H_{23}]^{3-}$ is the only known[22] oxidation product of $[B_{12}H_{12}]^{2-}$, it is suggested that the photoredox reaction proceeds according to Eq. (*1*).

$$2\{[Co(NH_3)_6]^{3+}[B_{12}H_{12}]^{2-}\} \xrightarrow{h\nu} 2\ Co^{2+} + 12\ NH_3 + [B_{24}H_{23}]^{3-} + H^+ \quad (1)$$

Generally, the redox centres in ion pairs interact only weakly; the Hush model[23,24] is then applicable. The theoretical half-bandwidth of the OSCT absorption should satisfy Eq. (*2*),

$$\Delta\bar{\nu}_{1/2} = [2\,310(E_{opt} - \Delta E)]^{1/2}\ , \quad (2)$$

E_{opt} (or $\Delta\bar{\nu}_{max}$) and ΔE being the energies of the OSCT transition at the absorption maximum and the potential difference between both redox pairs, respectively. $[Co(NH_3)_6]^{3+}$ is reduced at $E_{1/2}$ = –0.26 V *vs* SCE (ref.[25]). However, this potential is associated with the high-spin ground state of $[Co(NH_3)_6]^{2+}$. It is lower by 0.82 V for the low-spin form which is directly formed in the optical OSCT transition[26]. The value $E_{1/2}$ = –1.08 V *vs* SCE is then used for the $[Co(NH_3)_6]^{3+/2+}$ pair. $[B_{12}H_{12}]^{2-}$ is oxidized at $E_{1/2}$ = +1.50 V *vs* SCE (ref.[22]). Accordingly, the potential difference for the electron transfer from $[B_{12}H_{12}]^{2-}$ to $[Co(NH_3)_6]^{3+}$ amounts to 2.58 V. This value should be only taken as approximation owing to the irreversible oxidation of $[B_{12}H_{12}]^{2-}$ (ref.[22]). The theoretical half-width of $\Delta\bar{\nu}_{1/2}$ = 6 660 cm^{-1} is somewhat smaller than the experimental value (6 800 cm^{-1}), but the agreement is still remarkable.

The reorganization energy χ, associated with the electron transfer in the ion pair $[Co(NH_3)_6]^{3+}[B_{12}H_{12}]^{2-}$, is obtained from Eq. (*3*).

$$\chi = E_{opt} - \Delta E \quad (3)$$

The value of χ ≈ 19 200 cm^{-1} (67 kcal) is rather high. This is largely explained by the structural change that accompanies the reduction of

$[Co(NH_3)_6]^{3+}$ (ref.[27]). However, the oxidation of $[B_{12}H_{12}]^{2-}$ may also contribute to the large reorganization energy. Since the HOMO of $[B_{12}H_{12}]^{2-}$ is four-fold degenerate[28,29], the one-electron oxidation product $[B_{12}H_{12}]^{-}$ should undergo a Jahn–Teller distortion[29].

In the context of the present results, other observations are also of interest. Cations with strong polarizing properties, such as Ag^+, Cu^+ and Hg^{2+}, also interact with $[B_{12}H_{12}]^{2-}$ and $[B_{10}H_{10}]^{2-}$ (ref.[15]), although the nature of this interaction does not seem to be clear. Moreover, while pyridinium, 2,2′-dipyridinium and quinolinium salts of $[B_{12}H_{12}]^{2-}$ are colorless, those of $[B_{10}H_{10}]^{2-}$ are yellow to orange[15]. The origin of these colours is ascribed to CT bands. These observations are consistent with the fact that $[B_{10}H_{10}]^{2-}$ is much more prone to oxidation than $[B_{12}H_{12}]^{2-}$.

Another intriguing aspect of the present study relates to hydride ligands as inner-sphere CT donors. Do hydride complexes of oxidizing metals display ($H^- \rightarrow$ metal) LMCT absorptions in their electronic spectra? For example, the complex $[ReH_9]^{2-}$ was reported to show such an absorption at $\lambda_{max} = 217$ nm (refs[30,31]), but the nature of this band remains questionable[32]. Moreover, the electronic spectrum of the addition compound $(i\text{-}C_3H_7C_5H_4)_2WH_2$–phenanthrene-9,10-quinone contains a band which is attributed to an OSCT transition from the hydrido complex to the quinone[33,34]. However, the nature of the donor orbital is not clear. It may be a d orbital rather than a MO derived from the hydride ligands. The ion pair $[Co(NH_3)_6]^{3+}[B_{12}H_{12}]^{2-}$ seems to be the first well-documented example of a CT interaction of a coordination compound involving a hydride donor.

In summary, it has been shown that $[B_{12}H_{12}]^{2-}$ is a weak electron donor for OSCT transitions. Moreover, photooxidation of $[B_{12}H_{12}]^{2-}$ by the OSCT excitation is indicated.

Support of this research by the Fonds der Chemischen Industrie is gratefully acknowledged.

REFERENCES

1. Vlček A. A. in: *Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds* (A. J. McCleverty and J. A. Pombeiro, Eds), p. 3. Kluwer Academic Publishers, Dordrecht 1993.
2. Vlček A. A.: *Prog. Inorg. Chem.* **1963**, *5*, 211.
3. Vlček A. A.: *Collect. Czech. Chem. Commun.* **1960**, *25*, 2685.
4. Vogler A., Kunkely H.: *Top. Curr. Chem.* **1990**, *158*, 1.
5. Billing R., Rehorek D., Hennig H.: *Top. Curr. Chem.* **1990**, *158*, 151.
6. Vlček A. A.: *Coord. Chem. Rev.* **1982**, *43*, 39.
7. Housecraft C. E., Fehlner T. P.: *Adv. Organomet. Chem.* **1982**, *21*, 57.

8. Grimes R. N.: *Metal Interactions with Boron Clusters*. Plenum Press, New York 1982.
9. Kennedy J. D.: *Prog. Inorg. Chem.* **1984**, *32*, 519.
10. Kennedy J. D.: *Prog. Inorg. Chem.* **1986**, *34*, 211.
11. Housecroft C. E.: *Boranes and Metalloboranes*. Ellis Horwood, New York 1994.
12. Kunkely H.: Unpublished results.
13. Rehorek D., Schmidt D., Hennig H.: *Z. Chem.* **1980**, *20*, 223.
14. Pitochelli A. R., Hawthorne M. F.: *J. Am. Chem. Soc.* **1960**, *82*, 3228.
15. Muetterties E. L., Balthis J. H., Chia Y. T., Knoth W. H., Miller H. C.: *Inorg. Chem.* **1964**, *3*, 444.
16. Middaugh R. L. in: *Boron Hydride Chemistry* (E. L. Muetterties, Ed.), p. 273. Academic Press, New York 1975.
17. Schleyer P. von Rague, Najafian K.: *Inorg. Chem.* **1998**, *37*, 3454; and references therein.
18. Takano K., Izuho M., Hosoya H.: *J. Phys. Chem.* **1992**, *96*, 6962.
19. Kitson R. E.: *Anal. Chem.* **1959**, *22*, 664.
20. Lever A. B. P.: *Inorganic Electronic Spectroscopy*. Elsevier, Amsterdam 1974.
21. Hoffmann R., Lipscomb W. N.: *J. Chem. Phys.* **1962**, *37*, 2872.
22. Wiersema R. J., Middaugh R. L.: *Inorg. Chem.* **1969**, *8*, 2074.
23. Hush N. S.: *Prog. Inorg. Chem.* **1967**, *8*, 391.
24. Brown D. B.: *Mixed Valence Compounds*. Reidel, Dordrecht 1980.
25. Bond A. M., Lawrance G. A., Lay P. A., Sargeson A. M.: *Inorg. Chem.* **1983**, *22*, 2010.
26. Billing R., Benedix R., Stich G., Hennig H.: *Z. Anorg. Allg. Chem.* **1990**, *583*, 157.
27. Newton M. D.: *J. Phys. Chem.* **1991**, *95*, 30.
28. Longuett-Higgins H. C., Roberts M. De V.: *Proc. R. Soc. London, Ser. A* **1955**, *230*, 110.
29. Fujimori M., Kimura K.: *J. Solid State Chem.* **1997**, *133*, 178.
30. Abrahams S. C., Ginsberg A. P., Knox K.: *Inorg. Chem.* **1964**, *3*, 558.
31. Vogler A., Kunkely H.: *Comments Inorg. Chem.* **1997**, 19, 283.
32. Kunkely H., Vogler A.: *Transition Met. Chem. (London)* **1998**, *23*, 527.
33. Nakamura A., Otsuka S.: *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3641.
34. Kunkely H., Vogler A.: *Inorg. Chem. Commun.* **1998**, *1*, 200.