Preparation, Luminescence Studies, and Solution Behaviour of a Cerium–Tungsten Heterobimetallic Compound

Paulette N. Hazin,[a] **John C. Huffman,**[b] **and Joseph W. Bruno**[a]*

[a] *Hall-Atwater Laboratories, Wesleyan University, Middletown, Connecticut 06457, U.S.A.*
[b] *Molecular Structure Center, Indiana University, Bloomington, Indiana 47405, U.S.A.*

The crystal structure determination of cerium–tungsten compound (**2**) $[Cp''_2Ce\text{-}(\mu\text{-}OC)W(CO)(Cp)(\mu\text{-}CO)]_2$ [Cp″ = $C_5H_3(SiMe_3)_2$, Cp = C_5H_5] shows it to consist of a 12-membered ring in which Ce and W centres are linked by Σ-carbonyls; intact (**2**) is virtually non-emissive (presumably due to cerium–tungsten excited state energy transfer), but in acetonitrile solvent it serves as a source of the luminescent cerium cation $[Cp''_2Ce(NCMe)_x]^+$.

As part of a study of the synthetic and luminescent properties of organocerium(III) compounds, we recently reported the preparation of the cerium–tungsten heterobimetallic salt $[K(THF)_x][(C_5Me_5)_2Ce(I){-}O{=}C{-}W(CO)_2(C_5H_5)]$ (**1**), (THF = tetrahydrofuran) *via* the reaction shown in equation 1.[1] We also noted that the O-bound tungsten moiety is labile and dissociates to give the neutral cerium(III) compound $(C_5Me_5)_2Ce(I)(NCMe)_2$ in acetonitrile. In the course of these studies, we sought the 1,3-$C_5H_3(SiMe_3)_2$ (Cp″)[2,3] analogue of (**1**) for reasons of solubility. As such, $CeI_3(THF)_x$ was treated sequentially with Cp″K and $[K][CpW(CO)_3]$ (Cp = C_5H_5) to give Ce–W compound (**2**), equation 2. Isolated product (**2**) did not exhibit a solid-state (Nujol) infrared spectrum typical of C_s local symmetry in a $Cp(CO)_2W{-}C{=}O{-}Ce$ compound;[4] in particular, the low energy band (*ca.* 1646 cm^{-1}) was very broad and consisted of overlapping absorptions.

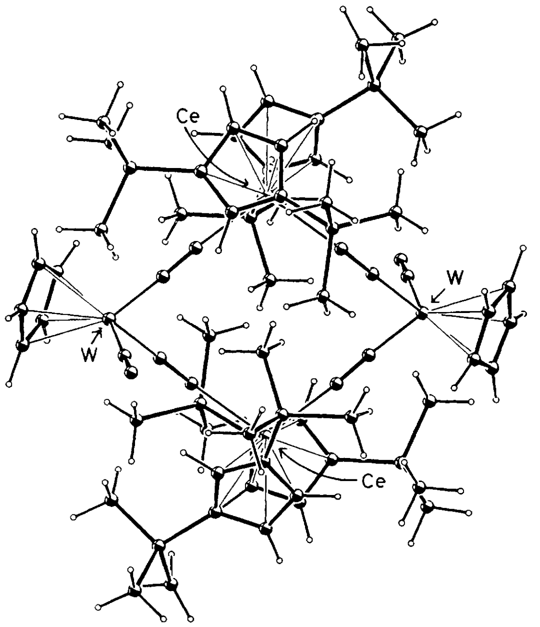

Figure 1. ORTEP drawing of the molecular structure of (2) with a view approximately perpendicular to the 12-membered ring.

$$[K(THF)_2][(C_5Me_5)_2CeI_2] + [K][CpW(CO)_3] \xrightarrow[\text{THF}]{} (\mathbf{1}) + KI \qquad (1)$$

$$2\,CeI_3(THF)_x \xrightarrow{4\,Cp''K} \xrightarrow{2\,[K][CpW(CO)_3]} (\mathbf{2}) + 6\,KI \qquad (2)$$

The *X*-ray structure† (Figure 1) indicates that dimeric (**2**) $[Cp''_2Ce\text{-}(\mu\text{-}OC)W(CO)(Cp)(\mu\text{-}CO)]_2$ forms with the loss of all iodide ligands and that the extra cerium co-ordination site is filled by a second tungsten carbonyl oxygen. The result is the

---

† *Crystal data* for (**2**): $Ce_2W_2C_{60}H_{94}Si_8O_6$, $M = 1784.03$, triclinic, $P\bar{1}$, $a = 13.579(3)$, $b = 23.043(6)$, $c = 12.928(3)$ Å, $\alpha = 93.76(1)$, $\beta = 111.62(1)$, $\gamma = 85.25(2)°$, $U = 3745.11$ Å^3, $Z = 2$, $D_c = 1.582$ g cm^{-3}. A total of 10511 reflections were collected to $2\theta = 45°$, of which 9630 had $F_o > 3\sigma(F_o)$. The data were solved using a combination of direct methods (MULTAN78) and Fourier techniques. Some, not all, hydrogens were located from a difference Fourier map, and hydrogen positions were fixed at d(C–H) = 0.95 Å for final cycles of refinement. The final residual was $R_w(F) = 0.0782$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

12-membered ring in which both of the tungstens utilize two carbonyl groups in bridging to cerium; it is unusual[5] for one metal centre to utilize two carbonyls in this way since formation of one such bridge has the effect of withdrawing electron density from the remaining carbonyls. One result of the double bridging is that there are relatively slight differences in the metrical parameters for bridging *versus* terminal carbonyls. For the two centrosymmetric molecules in the unit cell, the C–O bond lengths average 1.160 Å (terminal) and 1.182 Å (bridging), while the W–C lengths average 1.964 Å (terminal) and 1.895 Å (bridging). The bridging carbonyls are nearly linear at carbon (average W–C–O angle 178°), whereas the terminal carbonyls show *more* bending (average W–C–O angle 172.7°). Two of the oxygen atoms adopt a non-linear approach to cerium (average C–O–Ce angle 154.4°) while the others are more nearly linear (average C–O–Ce angle 174.8°). This gives the 12-membered rings a decided pucker, and a side view indicates a chair-like conformation.

Since anionic derivatives like (**1**) exhibit tungsten lability,[1] we chose to study the solution behaviour of the neutral analogue (**2**); this was facilitated by the use of luminescence and infrared spectroscopies. Cerium(III) compounds normally exhibit efficient luminescence out of an f-d excited state whose energy is sensitive to the nature of the cerium environment.[6] In contrast, the heterobimetallic compound (**2**) is non-emissive in the solid state or in THF or toluene solutions. Although we cannot eliminate excited state distortion as the non-radiative quenching pathway, we are inclined to discount it since we have not observed it for any other Cp_2CeXL co-ordination spheres; moreover, the ring system in (**2**) should make such distortions difficult. A quenching mechanism which is consistent with our data is the Förster-type energy transfer, operating in the weak coupling limit.[7] Using the absorption spectrum for CpW(CO)_3 moieties and the emission spectra of model $\text{Cp}''_2\text{Ce–X}$ compounds, we can integrate the spectral overlap and use the integrated area to calculate a value for R_o, the critical Ce–W distance at which the rate constants for emission and energy transfer are equal.[8] This number falls in the range 10—12 Å and our solid state structure indicates Ce–W separations of *ca.* 5 Å; as such, the Förster treatment predicts that an excited cerium centre would be efficiently quenched by the tungsten centres in the molecule. To verify that Ce–Ce interactions are not important in the quenching process, we prepared an analogue of (**2**) in which one Ce site was replaced with La (using a 4 : 1 ratio of La and Ce starting materials, random statistics would lead to 64% La–La, 32% Ce–La, and 4% Ce–Ce compounds); this Ce–La compound was also non-emissive. However, when (**2**) is dissolved in MeCN, it emits strongly with an emission maximum of 570 nm and a lifetime of 86 ns. This emission is due to the cationic $[\text{Cp}''_2\text{Ce(NCMe)}_x]^+$, equation 3, the presence of which was also indicated by i.r. {bands at 1892 and 1773 cm^{-1} indicate local C_{3v} symmetry at a symmetrically solvated $[\text{CpW(CO)}_3]^-$}.[4] Luminescence spectroscopy is thus a valuable analytical probe of Ce^{III} compounds in solution.

$$(\mathbf{2})\ \underset{\text{MeCN}}{\rightleftarrows}\ 2[\text{Cp}''\text{Ce(NCMe)}_x]^+ + 2[\text{CpW(CO)}_3]^- \qquad (3)$$

Finally, we note that the lability of the tungsten moiety in (**2**) can be exploited in the synthesis of other cation equivalents. Treatment of (**2**) with AgBF_4 results in the preparation of $\text{Cp}''_2\text{Ce(BF}_4)$ (**3**) and known $\{[\text{Ag}][\text{CpW(CO)}_3]\}_x$,[9] which can be separated by hexane extraction. Variable temperature ^{19}F n.m.r. studies in $[^2\text{H}_8]$toluene of the bonding mode of the BF_4 moiety in (**3**) were inconclusive; the spectrum contained a slightly broadened singlet which exhibited Curie–Weiss behaviour, but showed no evidence of decoalescence down to −70 °C (this question is still under study). In more polar solvents such as MeCN and THF, luminescence spectroscopy indicated the presence of substantial amounts of BF_4^- dissociation; in MeCN the luminescence spectrum of (**3**) is identical with that of (**2**), consistent with the identification of cationic $[\text{Cp}''_2\text{Ce(NCMe)}_x]^+$ as the emitting moiety. As such, compounds (**2**) and (**3**) are useful cation precursors in that they are soluble in solvents like toluene and hexane;[10] thus, they are readily separated from a range of inorganic by-products. In more polar solvents they result in significant proportions of cationic organolanthanide, and we are currently probing the chemistry of (**2**) and (**3**) and related compounds.

$$(\mathbf{2}) + 2\,\text{AgBF}_4 \rightarrow 2\,\text{Cp}''_2\text{Ce(BF}_4) + \tfrac{2}{x}\,\{[\text{Ag}][\text{CpW(CO)}_3]\}_x \qquad (4)$$

We thank Professor Joseph Knee for measuring the luminescence lifetimes and acknowledge financial support of this work by 3M Company.

Received, 9th May 1988; Com. 8/01799I

References

1 P. N. Hazin, C. Lakshminarayan, L. S. Brinen, J. L. Knee, J. W. Bruno, W. E. Streib, and K. Folting, *Inorg. Chem.*, 1988, **27**, 1393.

2 M. F. Lappert, A. Singh, J. L. Atwood, and W. E. Hunter, *J. Chem. Soc., Chem. Commun.*, 1981, 1190; M. F. Lappert, A. Singh, J. L. Atwood, and W. E. Hunter, *ibid.*, 1981, 1191

3 P. B. Hitchcock, M. F. Lappert, and M. J. Michalczyk. *J. Chem. Soc., Dalton Trans.*, 1987, 2635.

4 C. P. Horowitz and D. F. Shriver. *Adv. Organomet. Chem.*, 1984, **23**, 219; M. Y. Darensbourg. *Prog. Inorg. Chem.*, 1985, **33**, 221.

5 Only two examples are known; A. J. Conway, G. J. Gainsford, R. R. Schrieke, and J. D. Smith. *J. Chem. Soc., Dalton Trans.*, 1975, 2499; J. M. Boncella and R. A. Andersen, *Inorg. Chem.*, 1984, **23**, 432.

6 R. J. Lang, *Can. J. Res., Sect. A*, 1936, **14**, 127; L. Brewer, *J. Opt. Soc. Am.*, 1971, **61**, 1666; M. H. Crozier. *Phys. Rev. Sect. A*, 1965, **137**, 1781; E. Loh, *Phys. Rev.*, 1966, **147**, 332; G. Blasse and A. Bril. *J. Chem. Phys.*, 1967, **47**, 5139; G. Blasse and A. Bril. *Appl. Phys. Lett.*, 1967, **11**, 53; G. Blasse and A. Bril. *Philips Tech. Rev.*, 1970, **31**, 304; P. N. Hazin, J. W. Bruno, and H. G. Brittain, *Organometallics*, 1987, **6**, 913.

7 Th. Förster, in 'Modern Quantum Chemistry,' part 2, ed. O. Sinanoglu. Academic Press, New York, 1965, pp. 93—137.

8 The treatment is discussed in: W. DeW. Horrocks, Jr., B. Holmquist, and B. L. Vallee. *Proc. Natl. Acad. Sci. USA*, 1975, **72**, 4765; W. DeW. Horrocks, Jr. and M. Albin. *Prog. Inorg. Chem.*, 1984, **31**; G. Blasse, G. J. Dirksen, N. Sabbatini, and S. Perathoner, *Inorg. Chim. Acta*, 1987, **133**, 167.

9 P. Hackett and A. R. Manning. *J. Chem. Soc., Dalton Trans.*, 1975, 1606.

10 BF_4^- has been used as a weak ligand in transition metal chemistry: W. Beck and K. Schloter, *Z. Naturforsch*, 1978, **33**, 1214; M. Appel, W. Sacher, and W. Beck, *J. Organomet. Chem.*, 1987, **322**, 351, and references therein.