Structure and Vibrational Spectra of Trinuclear Metal Cluster Complexes. A Question of Symmetry

Akihiro Ohto, Ayako Tokiwa-Yamamoto,[1] Masaaki Abe,† Tasuku Ito, Yoichi Sasaki,*†† Keisuke Umakoshi,††
and Roderick D. Cannon*†††
Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980
†*Institute for Molecular Science, Okazaki 444*
††*Department of Chemistry, Faculty of Science, Hokkaido University, Kita-ku, Sapporo 060*
†††*School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, England*

(Received October 11, 1994)

Symmetry of the oxo-centered tri-ruthenium(III) complexes, $[Ru_3(O)(OOCR)_6(L)_3]^+$ (R = CH_3, C_6H_5; L = pyridine, H_2O), is discussed on the basis of the shapes of $\nu_{as}(OCO)$ bands in infra-red spectra, using comparisons between these complexes and related tri-rhodium(III) and mixed-metal Ru(III)$_2$M complexes. It is suggested that the tri-ruthenium(III) complexes have non-threefold symmetry.

The detailed structures of complexes containing the structural units $M_2M'(O)(OOCR)_6L_3$ are of great interest at present.[2] In cases where the trinuclear cluster contains mixed valencies such as 2M(III) + M'(II), the main point of discussion has been the extent and timescale of localisation of the extra electron. A fully delocalised electron configuration requires threefold symmetry, i.e. an equilateral triangle of metal atoms, and conversely, when the structure is significantly non-equilateral, the electron is at least partially localised. Homonuclear homovalent clusters $[M^{III}_3(O)(OOCR)_6L_3]^+$ are generally close to equilateral, and have in fact been used as standards by which to measure deviations from symmetry in other types of cluster.[3-5] Although crystal structures of such complexes often show non-threefold symmetry, the deviations are always small and usually have not been thought to be significant. Recently however it has been suggested[6,7] that in general, when the metal ions have unpaired electrons, structural deviations may be driven by electronic forces related to spin frustration.

The mixed-metal complexes involving second-row transition metals recently reported,[8-10] provide excellent data for a study of this effect. Here we show that simple observations of the infra-red spectra already give indication of symmetry lowering in the paramagnetic tri-ruthenium(III) clusters.

Spectra of the eight mixed-metal complexes $[Ru^{III}_2M^{II}(O)(OOCCH_3)_6L_3]$ (M = Mn, Co, Ni, Zn; L = C_5H_5N, H_2O)[8,9] are shown in Figure 1. The asymmetric carboxylate stretch $\nu_{as}(OCO)$ at ca. 1620 cm^{-1} shows a splitting in every case. Resolution increases in the order M = Mn < Co < Zn < Ni. The splitting is explained by the fact that the six carboxylate ions in each cluster are of distinct structural types, two of them bridging

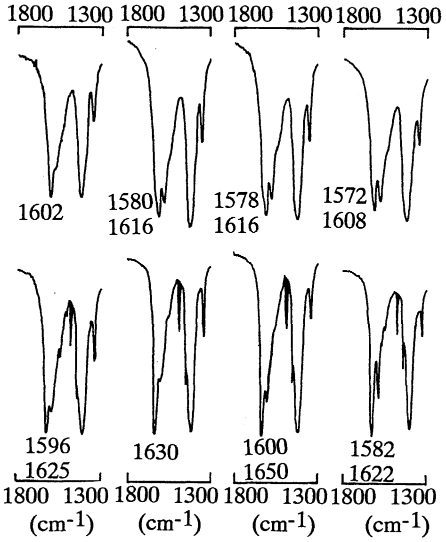

Figure 1. IR spectra, 1800 - 1300 cm^{-1} of complexes $[Ru^{III}_2M^{II}(O)(OOCCH_3)_6(H_2O)_3]$ and $[Ru^{III}_2M^{II}(O)(OOCCH_3)_6(py)_3](py)$. Left to right: M = Mn, Co, Zn, Ni. Upper series, H_2O complexes; lower series, py complexes. KBr discs, room temperature. Sharp bands shaded in black are assigned to vibrations of the pyridine molecules.

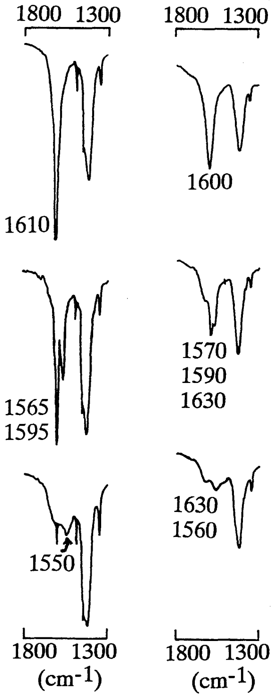

Figure 2. IR spectra, 1800 - 1300 cm^{-1} of complexes $[Rh^{III}_nRu^{III}_{3-n}(O)(OOCCH_3)_6(py)_3]ClO_4$ and $[Rh^{III}_nRu^{III}_{3-n}(O)(OOCCH_3)_6(H_2O)_3]ClO_4$. Top to bottom: n = 3, 1, 0. Left hand side, py complexes; right hand side, H_2O complexes. KBr discs, room temperature. Sharp bands shaded in black are assigned to vibrations of the pyridine molecules.

two identical metal ions, four of them bridging different atoms. As with some of the iron(III)-M(II) analogues,[11] the X-ray structure of the Ru_2Ni complex shows trigonal symmetry,[9] but this must be due to rotational disorder of the trinuclear units.[12,13]

Spectra of homovalent complexes $[Rh^{III}{}_nRu^{III}{}_{3-n}(O)(OOCCH_3)_6L_3]^+$ (n = 0, 1, 3),[10] are shown in Figure 2. We have measured two series of complexes, with L = C_5H_5N and L = H_2O, and they both show the same pattern, as follows. In the diamagnetic tri-rhodium(III) complexes, ν_{as}(OCO) is a single strong line. In the mixed-metal complexes, ν_{as}(OCO) has two well resolved components. In the tri-ruthenium(III) complex, ν_{as}(OCO) is split and also broadened significantly, as compared with the other spectra and with other nearby bands in the same spectra (In the series with L = pyridine, the spectra are complicated by the presence of the sharp weak bands at ca. 1600 and 1485 cm^{-1}, C-C stretches of pyridine, but the comparisons are still clear). When first reported,[14] the form of the tri-ruthenium(III) spectrum was noted as "anomalous" but the new data strongly suggest that it is due to a lowering of symmetry of the $[Ru_3O]$ cluster.

Crystal structures are available for three tri-ruthenium(III),[15,16] and two tri-rhodium(III) clusters.[17] In all of them, the complexes are located on general sites. Thus the three metal ions are not crystallographically equivalent, and it could be argued that this is the sole reason for the spectroscopic splittings. But the sharp single line of ν_{as}(OCO) in the tri-rhodium(III) complex contrasted with the broad bands in the tri-ruthenium(III) complexes suggests that other factors are involved as well. Moreover, the tri-ruthenium(III) complex $[Ru^{III}{}_3(O)(OOCC_6H_5)_6(py)_3]PF_6$ crystallises in the space group $P6_3$ with the complex ions in the point group C_3.[18] Yet in the IR spectrum ν_{as}(OCO) is split and broadened in just the same way. It seems clear that in this case at least, the cluster is subject to a distortion which is intrinsic to the molecule and is not driven by crystal packing forces, but in the room-temperature crystal structure the distortion is concealed by either static or dynamic disorder.

Recent neutron scattering data suggest that electronically-driven symmetry lowering effects occur in complexes of the clusters $Cr^{III}{}_3$[6] and $Fe^{III}{}_3$.[7] The evidence is a splitting of the electronic ground state S = 1/2, which was shown to occur in at least two cases in which the room-temperature X-ray crystal structure shows threefold rotational symmetry.[7] The effect has been rationalised in terms of spin frustration in the coupling scheme for these weakly antiferromagnetic systems, in line with an earlier prediction of a "magnetic Jahn-Teller effect".[19] In ligand-bridged clusters of second and third-row transition metals, metal-metal interactions are considered to be much stronger, and electronic structures have been rationalised in terms of molecular orbital scheme.[2] If the symmetry lowering which we propose here is real, it implies that the electronic ground state of the tri-ruthenium cluster is of the E type, in idealised threefold symmetry, and thus spontaneously distorts. It must be admitted that an existing orbital scheme for trimetallic clusters suggests that the highest occupied MO is of a_2' type symmetry[16,20,21] and would not lead to a Jahn-Teller effect. However the evidence pointed out here suggests that this could be reconsidered. Further experiments will also be required, to search for spectral splittings in other frequency ranges and at lower temperatures.

This work was supported by Grant-in-Aid for Scientific Research No. 05403008 and 05235202 (Priority Area of "Activation of Inactive Small Molecules") from the Ministry of Education, Science, and Culture, Japan. A research grant from Mitsubishi Foundation, and travel grant (to R.D.C) from the Royal Society and the British Council, are gratefully acknowledged.

References and Notes

1 Present address: Superconductivity Research Laboratory, International Superconductivity Technology Center, Shinonome, Koto-ku, Tokyo 135.

2 R. D. Cannon and R. P. White, *Prog. Inorg. Chem.*, **36**, 195 (1988).

3 R. D. Cannon, L. Montri, D. B. Brown, K. M. Marshall, and C. M. Elliot, *J. Am. Chem. Soc.*, **106**, 2591 (1984).

4 L. Meesuk, U. A. Jayasooriya, and R. D. Cannon, *J. Am. Chem. Soc.*, **109**, 2009 (1987).

5 L. Meesuk, R. P. White, B. Templeton, U. A. Jayasooriya, and R. D. Cannon, *Inorg. Chem.*, **29**, 2389 (1990).

6 U. A. Jayasooriya, R. D. Cannon, R. P. White, J. A. Stride, R. Grinter, and G. J. Kearley, *J. Chem. Phys.*, **98**, 9303 (1993).

7 R. D. Cannon, U. A. Jayasooriya, R. Wu, S. K. arapKoske, J. A. Stride, O. F. Nielson, R. P. White, G. J. Kearley, and D. Summerfield, *J. Am. Chem. Soc.*, in press.

8 a) A. Ohto, unpublished results (1991); b) Y. Sasaki, Y. Yoshida, A. Ohto, A. Tokiwa, T. Ito, H. Kobayashi, N. Uryû, and I. Mogi, *Chem. Lett.*, **1993**, 69.

9 A. Ohto, Y. Sasaki, and T. Ito, *Inorg. Chem.*, **33**, 1245 (1994).

10 Y. Sasaki, A. Tokiwa, and T. Ito, *J. Am. Chem. Soc.*, **109**, 6341 (1987).

11 A. B. Blake, A. Yavari, W. E. Hatfield, and C. N. Sethulekshmi, *J. Chem. Soc., Dalton Trans.*, **1985**, 2509.

12 Our proposal that the splitting is due to lowered symmetry of the cluster is supported by the fact that splitting seen in complexes of valency type $[Ru^{III}{}_2M^{III}]$, where M is a first transition metal, are smaller than in the present $[Ru^{III}{}_2M^{II}]$ complexes. The vibration ν_{as}(OCO) will be perturbed by coordination of the carboxylate group to the metal ions, and the difference in strength between Ru^{III}-O and M^{II}-O will be greater than the difference between Ru^{III}-O and M^{III}-O.

13 A referee has suggested that the differences in metal ion radii may also be relevant, but the effects on the C-O bonding are expected to be minor, and the difference in radii are also small: Ru^{3+}, 82 pm; Fe^{3+}, 79 pm; Mn^{2+}-Ni^{2+}, 97-83 pm (J. E. Huheey, E. A. Keiter, and R. L. Keiter, "Inorganic Chemistry," 4th ed, Harper Collins, New York (1993)).

14 M. K. Johnson, D. B. Powell, and R. D. Cannon, *Spectrochim. Acta*, **37A**, 995 (1981).

15 G. Powell, D. T. Richens, and A. K. Powell, *Inorg. Chim. Acta*, **213**, 147 (1993).

16 O. Almog, A. Bino, and D. Garfinkel-Shweky, *Inorg. Chim. Acta*, **213**, 99 (1993).

17 T. Glowiak, M. Kubiak, and T. Szymanska-Buzar, *Acta Crystallogr., Sect B: Struct. Crystallogr. Cryst. Chem.*, **B33**, 1732 (1977).

18 M. Abe, Y. Sasaki, T. Yamaguchi, and T. Ito, *Bull. Chem. Soc. Jpn.*, **65**, 1585 (1992).

19 T. Murao, *Phys. Lett.*, **49A**, 33 (1974).

20 F. A. Cotton and J. G. Norman, Jr., *Inorg. Chim. Acta*, **6**, 411 (1972).

21 J. A. Baumann, D. J. Salmon, S. T. Wilson, T. J. Meyer, and W. E. Hatfield, *Inorg. Chem.*, **17**, 3342 (1978).