Microwave Dielectric Loss and Dynamic Electron Delocalization in Trinuclear μ_3-Oxo-iron Clusters

Shamil' K. Shaikhutdinov

G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: +7 383 235 5756

Increased microwave dielectric loss in mixed-valence iron clusters has been observed and is attributed to dynamic electron delocalization.

During the last few years μ_3-oxo-clusters of general formula $[M_3O(RCOO)_6L_3]\cdot$solv have been investigated intensively due to their many interesting properties, in particular, the dynamic electron delocalization revealed by Mössbauer spectroscopy in mixed-valence $Fe^{III}_2Fe^{II}$ clusters (see refs. 1–4 and references therein). However, much less attention has been paid to their electronic properties. Recently we used a microwave dielectric loss (MDL) method on various 3d metal complexes and observed that MD losses are very sensitive towards the electronic and dimensional structure of the complexes.[5,6] Its mechanism has been attributed to an intramolecular polarization of the coordination centre. Thus, MDL investigations of clusters are believed to be of interest for both a determination of the nature of the losses in metal complexes and also the dynamics of electron transfer in clusters as well. We now report that MD losses in mixed-valence $Fe^{III}_2Fe^{II}$ clusters are significantly larger than in the corresponding Fe^{III}_3 clusters, provided dynamic electron delocalization has occurred.

Table 1 Some parameters for the iron clusters investigated.
(*a*) $[Fe^{III}_3O(RCOO)_6L_3]\cdot$solv

No.	R[a]	L	Solv	10^{-2} ε''	10^{-2} α'' /dm^3 mol^{-1}	Ref.[b]
I	Me	H_2O	NO_3 $2H_2O$	1.7	0.75	K$^+$ [1], [7]
II	Me	H_2O	NO_3 MeOH	1.2	0.55	D [10]
III	Ste	H_2O	NO_3	0.4	0.70	D [10]
IV	Pal	H_2O	NO_3	0.4	0.85	D [10]
V	Gly	H_2O	$(ClO_4)_7$	3.6	2.65	D$^+$ [9], [13]
VI	Me	$1.5\gamma,\gamma'$-dipy[c]	–	2.1	1.7	K [3], [7]
VII	CCl_3	$1.5\gamma,\gamma'$-dipy[c]	–	0.8	1.1	K [3], [7]
		$Fe^{III}(acac)_3$		0.2	0.05	from [5]
(*b*) $[Fe^{III}_2Fe^{II}O(RCOO)_6L_3]\cdot$solv						
VIII	Me	H_2O	$2H_2O$	5.5	2.5	K$^+$ [1]
IX	CCl_3	MeOH	$1.5H_2O$	9.0	7.5	K$^+$ [8], [12]
X	CF_3	H_2O	$3.5H_2O$	8.0	5.0	K$^+$ [11]
XI	Gly	H_2O	$(ClO_4)_6$	5.0	3.5	D [9]
XII	Gly	$(NH_3)_2CO$	$(ClO_4)_6$	5.0	3.5	D [9]

[a] Ste = $C_{15}H_{31}$; Pal = $C_{17}H_{35}$; Gly = $MeNH_2$; acac = acetylacetonate; dipy = dipyridyl. [b] Papers which include preparation conditions; letter 'K' and 'D' means samples from the Kishinev and Dushanbe groups, respectively. Superscript '+' means that the X-ray structure is known. [c] For these complexes $1.5\gamma,\gamma'$-dipy is considered as the L_3 ligand.

All complexes studied were prepared as described in refs. 7–10 by two investigating groups (see Acknowledgment and reference in Table 1). Measurements of the loss (ϵ'') at frequency 10 GHz at room temperature were performed as described elsewhere.[5] The mean-square errors did not exceed 20%. For equal experimental conditions the samples were dried under silica gel for two days and measurements were carried out in a nitrogen atmosphere. Since microwave dielectric properties in polycrystalline complexes with weak intermolecular interaction were attributed to the molecules themselves, we suggested[5] that proceeding with "specific" losses $\alpha'' = \varepsilon''/C$ (C is the molar concentration) would be more informative.

From Table 1 one can see that ε'' and α'' values in Fe^{III}_3 clusters are significantly larger than in mononuclear tris(acetylacetonato)iron(III) with a similar centre type, FeO_6. Moreover, their ratio for metal ions in molecules $\alpha''_{clust}/3\alpha''_{mono}$ is considerably larger than 1. This fact probably reflects the presence of exchange interaction in clusters. Therefore, MD losses in trinuclear clusters are connected with the electronic structure of the coordination cluster centre as a whole. This conclusion is favoured by the fact that the α'' values in complexes with acetate and stearate ligands I–V are approximately equal despite their appreciable differences in ε'' values which are caused by a lower concentration of the microwave absorbed Fe^{III}_3 centres in complexes with large R substituents.

MDL dependence on the nature of the ligand in clusters is similar in some ways to that observed in mononuclear ones.[5,6] Indeed, one can see that the introduction of a donor ligand results in increasing loss (*cf.* I and VI, Table 1) while an acceptor ligand decreases the loss (*cf.* VI and VII, Table 1). The higher values for clusters with glycine V may partly be a result of the various synthetic methods that have been observed[8] in mixed-valence clusters when studied by Mössbauer spectroscopy. So, similarly to mononuclear complexes, it is felt that the influence of the ligand on the loss values is connected with a redistribution of the electron density in the cluster which takes part in the MD polarization process.

In mixed-valence $Fe^{III}_2Fe^{II}$ complexes the losses depend significantly on the ligand nature. Indeed, a great increase in the α'' and ε'' values is found in complexes VIII–X with methyl and their halogen-substituted analogues but not with glycine XI–XII with respect to their corresponding Fe^{III}_3 clusters. It is reasonable to explain these results by dynamic delocalization processes in mixed-valence complexes. In fact, it is well known[1] that this phenomenon is based on the ratio between the characteristic time of the method used, τ_m, and the electron transfer time, τ_e. When $\tau_m > \tau_e$ an electron may be observed on one of the metal ions with equal probability, *i.e.* the electron is revealed as delocalized on the method's time scale. In the opposite case, $\tau_m < \tau_e$, the electron will be localized. Since τ_e is sharply lowered with increase in temperature there is a so-called delocalization temperature T_d at which $\tau_e \sim \tau_m$. From Mössbauer spectra[1,8,14,15] in complexes VII–X, T_d was found to be lower than 200 K. This means that at room temperature $\tau_e < \tau_m \approx 10^{-7}$ s, taking into account the Mössbauer time scale. By computer modelling of Mössbauer spectra τ_e was estimated[1] as *ca.* 10^{-9} s. Moreover, IR and Raman spectroscopy investigations[4] of complexes similar to VIII showed that the oxidation states are partially localized on the vibrational time scale *i.e.* $\tau_e > 10^{-12}$ s. Therefore, this is a good reason to suppose that the electron hopping frequency τ_e^{-1} is partly covered by the microwave region *ca.* 10^{10} s^{-1} used in the MDL method. Thus, it is believed that an increase of the MD losses in these mixed-valence clusters appear to be attributable to *intra*molecular electron hopping. Indeed, in complexes with glycine T_d was found[15] to be higher: 300 K. Hence, on the microwave time scale the "extra" electron is localized and does not contribute to the losses measured.

Although MDL measurements were performed in polycrystals some contribution of the dipole rotation loss was not entirely excluded *e.g.* from rest solvents which were not removed under drying or from the structured but mobile fragments of molecules, *e.g.* OH^- group. Nevertheless, preliminary studies showed that the ε'' values of these clusters depend slightly on temperature at 250–300 K. This means that at least dipole orientation losses are relatively small, if any.

Systematic investigations of MDL dependence on various ligands and their substituents as well as temperature seem to yield more information on the nature of dielectric loss in similar systems.

The author gratefully thanks Professor K. Turte and Dr. S. Bobkova (Institute of Chemistry, Kishinev, Moldova) and Drs. T. Nasonova and V. Fisher (Tajik State University, Dushanbe, Tajikistan) for kindly donating the complexes studied.

References

1 V. I. Goldanskii, V. P. Alekseev, R. A. Stukan, K. I. Turte and A. V. Ablov, *Dokl. Akad. Nauk SSSR*, 1973, **213**, 867 [*Dokl. Phys. Chem. (Engl. Transl.)*, 1973, **213**, 1063].

2 S. M. Oh, S. R. Wilson, D. M. Hendrickson, S. E. Woehler, R. J. Witterbort, D. Inniss and Ch. E. Strouse, *J. Am. Chem. Soc.*, 1987, **109**, 1073.

3 K. I. Turte, in *Poliyadernye Koordinatsionnye Soedineniya (Polynuclear Coordination Compounds)*, Tadzhikskii Gosudarstvennyi Universitet, Dushanbe, 1986, p. 43 (in Russian).

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

5 Sh. K. Shaikhutdinov, A. N. Shupik and E. M. Trukhan, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 3959.

6 Sh. K. Shaikhutdinov, A. N. Astanina, E. M. Trukhan, K. I. Turta, I. I. Bulgak and V. E. Zubareva, *Koord. Khim.*, 1987, **13**, 643 (in Russian).

7 R. A. Stukan, K. I. Turte, A. V. Ablov and S. A. Bobkova, *Koord. Khim.*, 1979, **5**, 95 (*Sov. J. Coord. Chem.*, 1979, **5**, 73).

8 K. I. Turte, S. A. Bobkova, R. A. Stukan and S. G. Shova, *Koord. Khim.*, 1981, **7**, 1682 (*Sov. J. Coord. Chem.*, 1981, **7**, 841).

9 V. R. Fisher, T. A. Nasonova, Kh. M. Yakubov, V. K. Voronkova, L. V. Mosina and Yu. V. Yablokov, *Zh. Neorg. Khim.*, 1990, **35**, 2279 (*Russ. J. Inorg. Chem.*, 1990, **35**, 1298).

10 Kh. M. Yakubov, G. L. Semenova and M. M. Mansurov, *Zh. Neorg. Khim.*, 1985, **30**, 368 (*Russ. J. Inorg. Chem.*, 1985, **30**, 206).

11 V. I. Ponomarev, O. S. Filipenko, L. O. Atovmian, S. A. Bobkova and K. I. Turte, *Dokl. Akad. Nauk SSSR*, 1982, **262**, 346 (in Russian).

12 V. I. Ponomarev, G. V. Shilov, L. O. Atovmian, K. I. Turte and S. A. Bobkova, *Koord. Khim.*, 1987, **13**, 1097 (*Sov. J. Coord. Chem.*, 1987, **13**, 617).

13 R. V. Thundathil, E. M. Holt, S. L. Holt and K. J. Watson, *J. Am. Chem. Soc.*, 1974, **99**, 1848.

14 K. I. Turte, S. A. Bobkova and R. A. Stukan, *Zh. Neorg. Khim.*, 1982, **27**, 954 (*Russ. J. Inorg. Chem.*, 1982, **27**, 535).

15 S. A. Bobkova, *Ph.D. Thesis*, Kishinev, 1982.

Received: Moscow, 24th May 1994
Cambridge, 7th July 1994; Com. 4/04140B