May, 1981] *Bull. Chem. Soc. Jpn.*, ***54***, *1375—1379 (1981)* 1375

The Temperature Dependence of the Trapped and Averaged-valence State in Mono-oxidized Dialkylbiferrocenes

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(Received August 4, 1980)

An interesting temperature dependence of the valence state was observed in the Mössbauer spectra of the mixed-valence salts of 1′,1‴-dialkylbiferrocenes, measured at various temperatures from 4.2 K to 300 K. A mechanistic consideration of the temperature dependence has been carried out assuming a conformational change of the monocation salts induced both by the variation in the temperature and by the kind of counter anion.

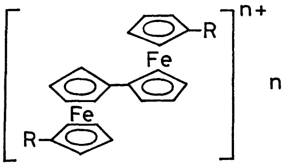
The monocation salts of binuclear ferrocenes are so-called "mixed-valence" compounds, in which, formally, two kinds of iron atoms, Fe(II) and Fe(III), are simultaneously contained. It is known that the monocation salts can be classified into two types, a trapped-valence type (or a mixed-valence type, in a narrow sense) and an averaged-valence one, by means of Mössbauer spectroscopy.[1–7] The former type gives two different states of irons, corresponding to bi- and tervalent irons, while the latter gives iron atoms in an equivalent state averaged between these two kinds of valence states. As for biferrocene derivatives, various monocation salts of biferrocene itself have been reported to be of the trapped-valence type,[1,4] while 1′,1‴-diiodobiferrocenium triiodide is of the averaged-valence type.[4]

In the present paper, results will be reported on the temperature dependence of valence states in mono-oxidized 1′,1‴-diethyl- and 1′,1‴-dipropylbiferrocenes[††] investigated by means of Mössbauer spectroscopy.

Results and Discussion

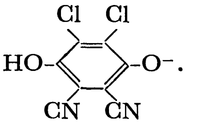
The biferrocene derivatives used in this study are listed in Table 1, all the compounds, **1**—**8**, were identified by means of elemental analyses (**1** and **5** were also identified by NMR), the results of which are summarized in Table 2. The Mössbauer data for the neutral species, 1′,1‴-diethylbiferrocene (**1**) and 1′,1‴-dipropylbiferrocene (**5**), are shown in Table 3, along with the data for unsubstituted biferrocene. The Mössbauer spectra of **1** and **5** at 78 K are shown in Fig. 1. The Mössbauer parameters of the substituted biferrocenes are actually identical to those of unsubstituted biferrocene at the same temperature, indicating that the replacement of hydrogens by alkyl groups does not affect the Mössbauer parameters of biferrocene.

Table 1. Compounds

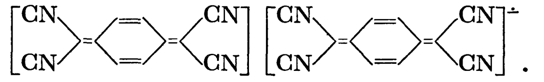


Compound	R	*n*	X$^-$
1′,1‴-Diethylbiferrocene (**1**)	C_2H_5	0	
1′,1‴-Diethylbiferrocenium$^+$I$_3^-$ (**2**)	C_2H_5	1	I_3^-
1′,1‴-Diethylbiferrocenium^{2+}(BF$_4^-$)$_2$ (**3**)	C_2H_5	2	BF_4^-
1′,1‴-Diethylbiferrocenium^{2+}(DDQH$^-$)$_2$ (**4**)	C_2H_5	2	DDQH$^-$ [a)]
1′,1‴-Dipropylbiferrocene (**5**)	C_3H_7	0	
1′,1‴-Dipropylbiferrocenium$^+$I$_3^-$ (**6**)	C_3H_7	1	I_3^-
1′,1‴-Dipropylbiferrocenium$^+$(TCNQ)$_2^{\cdot-}$ (**7**)	C_3H_7	1	(TCNQ)$_2^{\cdot-}$ [b)]
1′,1‴-Dipropylbiferrocenium^{2+}(BF$_4^-$)$_2$ (**8**)	C_3H_7	2	BF_4^-

a) DDQH$^-$≡



b) (TCNQ$_2$)$^{\cdot-}$≡



The Mössbauer parameters for the dication salts, 1′,1‴-diethylbiferrocenium^{2+}(BF$_4^-$)$_2$ (**3**), 1′,1‴-diethylbiferrocenium^{2+}(DDQH$^-$)$_2$ (**4**), and 1′,1‴-dipropylbiferrocenium^{2+}(BF$_4^-$)$_2$ (**8**), are listed in Table 4, along with those for biferrocenium^{2+}(BF$_4^-$)$_2$. The Mössbauer spectra of these dication salts, **3**, **4**, and **8** show broad singlet peaks with very small quadrupole splittings, which are assignable to the ferrocenium-like tervalent iron, although generally no quadrupole splittings are found in the Mössbauer spectra of most mononuclear ferrocenium salts.[8] The 78 K spectra of **3** and **8** are shown in Fig. 2. The Mössbauer parameters of the dications of the diethylbiferrocene, **3** and **4**, with BF$_4^-$ and DDQH$^-$ respectively as the counter ion, are essentially identical at the same temperature. Therefore, no effect of the counter anion was found on the parameters of these dication salts. These results agree with the fact that little difference can be detected in the Mössbauer parameters of mononuclear ferrocenium salts containing various anions as the counter ion.[8] Furthermore, the Mössbauer parameters of **3**, **4**, and **8** are quite similar to those of biferrocenium^{2+}(BF$_4^-$)$_2$ at the same temperature. Thus, no effect of the alkyl substitution was found on the Mössbauer parameters of the dications.

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[††] The proper name of this type of compound is 1′,1‴-dialkyl-1,1″-biferrocenyl according to the nomenclature followed by the tentative IUPAC rule.

Table 2. Analytical data

Compound	Calcd(%) C	Calcd(%) H	Found(%) C	Found(%) H
1′,1‴-Diethylbiferrocene (**1**)	67.64	6.15	67.67	6.39
1′,1‴-Diethylbiferrocenium$^+$$I_3^-$ (**2**)[a]	35.75	3.25	35.66	3.21
1′,1‴-Diethylbiferrocenium^{2+}$(BF_4^-)_2$ (**3**)	48.06	4.37	47.99	4.40
1′,1‴-Diethylbiferrocenium^{2+}$(DDQH^-)_2$ (**4**)[b]	54.46	3.20	54.90	3.40
1′,1‴-Dipropylbiferrocene (**5**)	69.36	7.12	68.75	6.66
1′,1‴-Dipropylbiferrocenium$^+$$I_3^-$ (**6**)	37.40	3.62	37.49	3.72
1′,1‴-Dipropylbiferrocenium$^+$$(TCNQ)_2^{\dot{-}}$ (**7**)[c]	69.62	4.44	69.59	4.52
1′,1‴-Dipropylbiferrocenium^{2+}$(BF_4^-)_2$ (**8**)	49.67	4.85	49.77	4.82

a) Iodine analysis: Calcd, 47.18%; Found, 47.39%. b) Nitrogen analysis: Calcd, 6.35%; Found, 6.40%. c) Nitrogen analysis: Calcd, 12.99%; Found, 13.00%.

Table 3. Mössbauer data for 1′,1‴-diethylbiferrocene (**1**), 1′,1‴-dipropylbiferrocene (**5**), and biferrocene

Compound	Temperature/K	δ[a]/mm s^{-1}	ΔE_Q/mm s^{-1}
1′,1‴-Diethylbiferrocene (**1**)	300	0.45	2.30
	78	0.55	2.34
1′,1‴-Dipropylbiferrocene (**5**)	300	0.44	2.30
	78	0.55	2.31
Biferrocene	298	0.45[b]	2.30[b]
		0.45[c]	2.30[c]
	78	0.55[b]	2.34[b]
		0.52[c]	2.36[c]

a) Isomer-shift data are reported with respect to metallic iron foil. b) See Ref. 9. c) See Ref. 17.

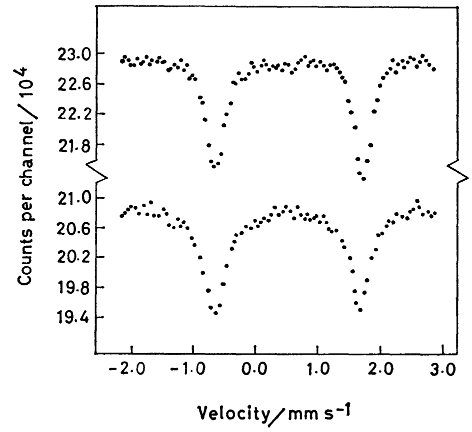

Fig. 1. Mössbauer spectra at 78 K of 1′,1‴-diethylbiferrocene (**1**) (top) and 1′,1‴-dipropylbiferrocene (**5**) (bottom).

Mössbauer measurements of the monocation salt, 1′,1‴-diethylbiferrocenium$^+$$I_3^-$ (**2**), were carried out at ten different temperatures between 4.2 to 300 K. The Mössbauer data for **2** are summarized in Table 5, along with those for the related compounds, while the spectrum at each temperature is shown in Figs. 3 and 4. As can be seen from Figs. 3 and 4, the shape of the spectrum greatly depends upon the temperature of the measurement. The spectrum at 4.2 K consists of inner and outer doublets in a nearly 1:1 ratio; these doublets are ascribed to the ferrocenium-like tervalent and ferrocene-like bivalent iron in **2** respectively. This spectrum is of the typical trapped-valence type. With an increase in the temperature, however, the quadrupole splitting of the inner doublet increases, while that of the outer doublet decreases gradually. Eventually, at 275 and 300 K, **2** shows typical averaged-valence spectra which consist of a single quadrupole doublet.

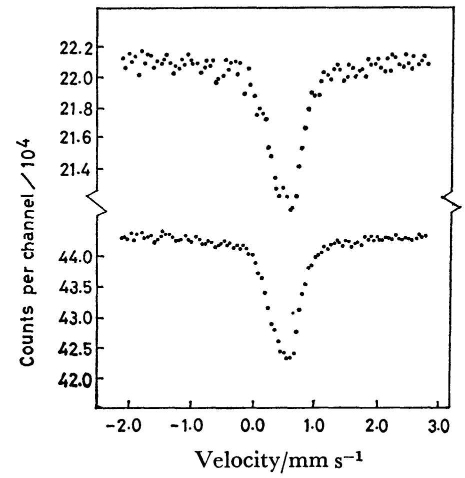

Fig. 2. Mössbauer spectra at 78 K of 1′,1‴-diethylbiferrocenium^{2+}$(BF_4^-)_2$ (**3**) (top) and 1′,1‴-dipropylbiferrocenium^{2+}$(BF_4^-)_2$ (**8**) (bottom).

The Mössbauer data for 1′,1‴-dipropylbiferrocenium$^+$$I_3^-$ (**6**), are summarized in Table 6. The temperature dependence of the Mössbauer spectra of **6** was found to be very similar to that of **2**, but the typical averaged-valence spectrum appears at a temperature

Table 4. Mössbauer data for 1′,1‴-diethylbiferrocenium^{2+}(BF_4^-)$_2$ (**3**), 1′,1‴-diethylbiferrocenium^{2+}($DDQH^-$)$_2$ (**4**), 1′,1‴-dipropylbiferrocenium^{2+}(BF_4^-)$_2$ (**8**), and biferrocenium^{2+}(BF_4^-)$_2$

Compound	Temperature/K	$\delta^{a)}$/mm s^{-1}	ΔE_Q/mm s^{-1}
1′,1‴-Diethylbiferrocenium^{2+}(BF_4^-)$_2$ (**3**)	78	0.54	0.17
1′,1‴-Diethylbiferrocenium^{2+}($DDQH^-$)$_2$ (**4**)	300	0.38	0.17
	78	0.48	0.17
1′,1‴-Dipropylbiferrocenium^{2+}(BF_4^-)$_2$ (**8**)	300	0.35	*ca.* 0.1
	78	0.54	0.14
Biferrocenium^{2+}(BF_4^-)$_2$	77	0.497$^{b)}$	0.163$^{c)}$

a) Isomer-shift data are reported with respect to metallic iron foil. b) See Ref. 1.

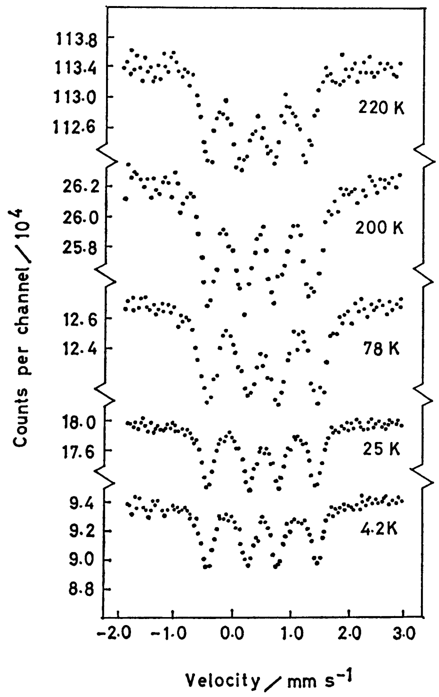

Fig. 3. Mössbauer spectra of 1′,1‴-diethylbiferrocenium$^+I_3^-$ (**2**) in the temperature range 4.2—220 K.

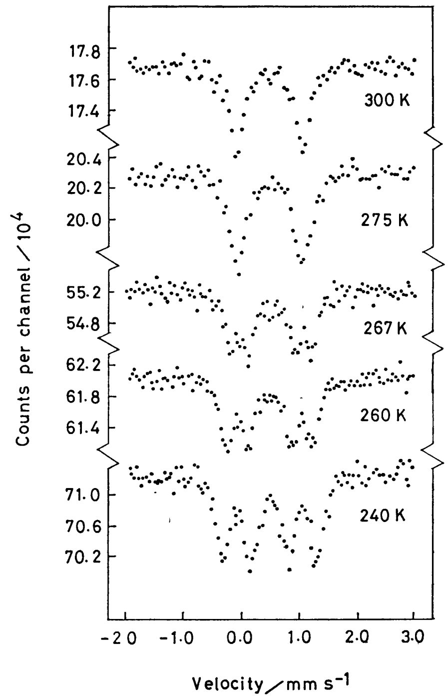

Fig. 4. Mössbauer spectra of 1′,1‴-diethylbiferrocenium$^+I_3^-$ (**2**) in the temperature range 240—300 K.

about 25—30 degrees lower than that in the case of **2**, as is shown in Fig. 5.

As was mentioned in the Introduction, the Mössbauer spectra of biferrocenium$^+I_3^-$ and 1′,1‴-diiodobiferrocenium$^+I_3^-$ are of the trapped-valence and averaged-valence types respectively, neither of which is temperature-dependent. Consequently, it is obvious that these monocation salts of the dialkylbiferrocenes, **2** and **6**, are an additional type of "mixed-valence" compound, the valence state of which changes from the trapped-valence state to the averaged-valence one with the elevation of the temperature. Furthermore, from the Mössbauer spectroscopic behavior of the four monocation salts just discussed above, it can be said that the valence state of the mono-oxidized biferrocene system is greatly affected by the kind of substituent on the biferrocene system, while little effect of the substitution is found on the Mössbauer parameters of the neutral and dioxidized species.

In previous papers we reported that the monocation salt of *as*-indacenebis(cyclopentadienyliron) was the first example of a binuclear ferrocene salt which shows a remarkably temperature-dependent Mössbauer spectrum, that is, a trapped-valence-type spectrum at a lower temperature and an averaged-valence-type one at higher temperature.[9,10] This temperature dependence was interpreted successfully in terms of an electron-hopping process, in which the thermal electron-transfer takes place between two iron atoms and the electron-transfer increases with the increase in the temperature. However, the behavior of **2** and **6** observed in this study cannot be explained by using such an electron-hopping process, because the line-broadening of the Mössbauer spectrum at intermediate temperatures, which is characteristic of such a process,[9,11–13] was not found for **2** and **6**. It was previously suggested that the difference in valence state between biferrocenium$^+I_3^-$ and 1′,1‴-diiodobiferrocenium$^+I_3^-$ was attributable to the conformational difference between these monocations.[4] It was also suggested that the diiodo-monocation is in a *trans* or *cis* conformation with respect to the iron atoms, which would enhance the interaction between the two iron centers. The change in valence state observed for **2** and **6** seems to be understandable according to the following assumptions regarding the monocations:

that the conformation of the monocation of **2**, as well as that of **6**, at low temperatures (below about 200 K for **2**) differs from that at high temperatures (above about 270 K for **2**), and that the latter conformation, probably similar to that of the diiodo-monocation, causes strong interaction between the two iron atoms, that is, a full delocalization of electrons between the iron centers. At an intermediate temperature, it can be concluded that the conformation of the 1′,1‴-diethylbiferrocenium and 1′,1‴-dipropylbiferrocenium monocation varies gradually from the low-temperature-type conformation to the high-temperature-type one with an increase in the temperature.

As indicated by the data cited in Table 6, the anion-substituted monocation salt of 1′,1‴-dipropylbiferrocene, 1′,1‴-dipropylbiferrocenium$^+$$(TCNQ)_2^{\dot{-}}$ (**7**), was found to give averaged-valence-type Mössbauer spectra, which are not temperature-dependent. As has been described above, we found little effect of anions on the Mössbauer parameters for the mononuclear ferrocenium salts; this was also demonstrated for the dioxidized 1′,1‴-diethylbiferrocene of Mössbauer spectra in the present work. The difference observed in the temperature dependence of the Mössbauer spectra between **6** and **7** may suggest that the conformation of the 1′,1‴-dipropylbiferrocenium mono-

Table 5. Mössbauer data for 1′,1‴-diethylbiferrocenium$^+$$I_3^-$ (**2**)

Temperature/K	$\delta^{a)}$/mm s^{-1}	ΔE_Q/mm s^{-1}	$\Gamma_{1/2}$/mm s^{-1}
300	0.47	1.17	0.27
275	0.47	1.16	0.33
267	0.46	0.87	0.29
	0.45	1.42	0.27
260	0.46	0.80	0.30
	0.46	1.51	0.29
240	0.46	0.68	0.31
	0.47	1.64	0.30
220	0.50	0.58	0.33
	0.50	1.72	0.30
200	0.49	0.56	0.34
	0.48	1.80	0.32
78	0.57	0.50	0.36
	0.55	1.88	0.32
25	0.54	0.52	0.36
	0.54	1.91	0.34
4.2	0.53	0.51	0.37
	0.54	1.93	0.35

a) Isomer-shift data are reported with respect to metallic iron foil.

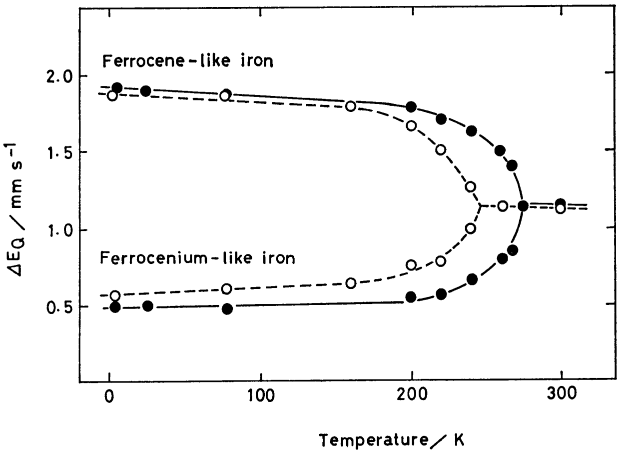

Fig. 5. Temperature-dependence of the quadrupole splittings of 1′,1‴-diethylbiferrocenium$^+$$I_3^-$ (**2**) and 1′,1‴-dipropylbiferrocenium$^+$$I_3^-$ (**6**).
—●—●— 1′,1‴-Diethylbiferrocenium$^+$$I_3^-$ (**2**),
—○—○— 1′,1‴-dipropylbiferrocenium$^+$$I_3^-$ (**6**).

Table 6. Mössbauer data for 1′,1‴-dipropylbiferrocenium$^+$$I_3^-$ (**6**) and 1′,1‴-dipropylbiferrocenium$^+$$(TCNQ)_2^{\dot{-}}$ (**7**)

Compound	Temperature/K	$\delta^{a)}$/mm s^{-1}	ΔE_Q/mm s^{-1}	$\Gamma_{1/2}$/mm s^{-1}
1′,1‴-Dipropylbiferrocenium$^+$$I_3^-$ (**6**)	300	0.44	1.16	0.25
	260	0.45	1.16	0.33
	240	0.46	0.97	0.27
		0.46	1.27	0.27
	220	0.47	0.78	0.32
		0.45	1.51	0.31
	200	0.49	0.75	0.32
		0.49	1.68	0.31
	160	0.50	0.64	0.33
		0.50	1.81	0.32
	78	0.54	0.60	0.34
		0.54	1.90	0.33
	4.2	0.54	0.57	0.35
		0.53	1.92	0.33
1′,1‴-Dipropylbiferrocenium$^+$$(TCNQ)_2^{\dot{-}}$ (**7**)$^{b)}$	300	0.45	0.84	0.31
	78	0.52	1.20	0.36
	4.2	0.55	1.27	0.43

a) Isomer-shift data are reported with respect to metallic iron foil. b) The presence of a small amount of the dioxidized species of 1,1‴-dipropylbiferrocene was detected.

cation in the crystalline state is considerably influenced by the counter ion and controls the extent of interaction between the metal centers.

Experimental

Mössbauer Measurements. As the radioactive source for Mössbauer measurements a ^{57}Co(Pt) moving in a constant-acceleration mode was used. The Mössbauer spectra of **2**, **5**, and **6** were obtained by using an Austin Science Associates Mössbauer spectrometer and a proportional counter. The other spectra were obtained by using a Shimadzu Mössbauer spectrometer and a NaI scintillator. The isomer shifts are determined relative to metallic iron foil. The experimental errors of the Mössbauer parameters are estimated to be ±0.03 mm/s.

Materials. The 1′,1‴-diethylbiferrocene **1** was prepared by the Ullmann coupling of 1-ethyl-1′-bromoferrocene,[14] which had itself been obtained from the $LiAlH_4$-$AlCl_3$ reduction of 1-acetyl-1′-bromoferrocene.[15]

The 1′,1‴-dipropylbiferrocene **5** was prepared by the Ullmann coupling of 1-propyl-1′-bromoferrocene, which had itself been obtained from the reduction of 1-propionyl-1′-bromoferrocene. 1-Propyl-1′-bromoferrocene (2.5 g, 8.1 mmol) mixed with 10 g of copper powder was heated to 120—130 °C for 18 h in a sealed glass tube. **5** was rapidly separated from the starting materials by using column chromatography on alumina; it was then obtained as reddish needles upon recrystallization from hexane. Mp 67—68 °C. ^{1}H NMR δ 0.90 (6H, t), 1.46 (4H, m), 2.16 (4H, t), 3.90 (8H, s), 4.16 (4H, t), and 4.30 (4H, t).

The 1′,1‴-dipropylbiferrocenium$^+$(TCNQ)$_2^{\dot{-}}$ (**7**) was synthesized according to the procedure used for the preparation of ferrocenium$^+$(TCNQ)$_2^{\dot{-}}$,[16] as follows. To a refluxing solution of 82 mg (0.4 mmol) of TCNQ in 30 ml of acetonitrile, a 91 mg portion (0.2 mmol) of **5** was added. After the reaction mixture had been refluxed for 15 min, **7** was separated out as blue-black needles, but in a low yield, on cooling. **5** did not react with TCNQ in boiling dichloromethane in place of acetonitrile.

The 1′,1‴-diethylbiferrocenium$^+I_3^-$ (**2**), 1′,1‴-diethylbiferrocenium$^{2+}(BF_4^-)_2$ (**3**), 1′,1‴-diethylbiferrocenium^{2+}-(DDQH$^-$)$_2$ (**4**), and 1′,1‴-dipropylbiferrocenium$^{2+}(BF_4^-)_2$ (**8**) were synthesized according to the procedures previously reported for the preparation of the corresponding salts of unsubstituted biferrocene.[1,2,4]

The analytical data for all the compounds described above are listed in Table 2.

References

1) D. O. Cowan, R. L. Collins, and F. Kaufman, *J. Phys. Chem.*, **75**, 2025 (1971).

2) W. H. Morrison, Jr., and D. N. Hendrickson, *J. Chem. Phys.*, **59**, 380 (1973).

3) W. H. Morrison, Jr., and D. N. Hendrickson, *Chem. Phys. Lett.*, **22**, 119 (1973).

4) W. H. Morrison, Jr., and D. N. Hendrickson, *Inorg. Chem.*, **14**, 2331 (1975).

5) I. Motoyama, M. Watanabe, and H. Sano, *Chem. Lett.*, **1978**, 513.

6) M. Watanabe, S. Iijima, I. Motoyama, and H. Sano, *J. Phys. (Paris), Colloq.*, **C2**, 392 (1979).

7) J. A. Kramer, F. H. Herbstein, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **102**, 2293 (1980).

8) See, for example, Ref. 5 and R. H. Collins, *J. Chem. Phys.*, **42**, 1072 (1965).

9) S. Iijima, I. Motoyama, and H. Sano, *Bull. Chem. Soc. Jpn.*, **53**, 3184 (1980).

10) S. Iijima, I. Motoyama, and H. Sano, *Chem. Lett.*, **1979**, 1349.

11) O. Berkooz, M. Malamud, and S. Shtrikman, *Solid State Commun.*, **6**, 185 (1968).

12) G. A. Sawatzky, J. M. D. Coey, and A. H. Morrish, *J. Appl. Phys.*, **40**, 1402 (1969).

13) D. Lupu, D. Barb, G. Filoti, M. Moratiu, and D. Tarina, *J. Inorg. Nucl. Chem.*, **34**, 2803 (1972).

14) A. N. Nesmeyanov, V. N. Dorzd, V. A. Sazonova, V. I. Romanenko, A. K. Prokof'ef, and L. A. Nikonova, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk*, **1962**, 47.

15) D. W. Hall and J. H. Richards, *J. Org. Chem.*, **28**, 1549 (1963).

16) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962).

17) G. K. Wertheim and R. H. Herber, *J. Chem. Phys.*, **38**, 2106 (1963).