철(III)-옥살산 착물의 합성과 규명에 관한 연구

崔奇珠 · 金明淳 · 孫蓮秀*

한국과학기술연구소

(1975. 10. 8 접수)

Synthesis and Characterization of Oxalatoferrate(III) Complexes

Kee Ju Choi, Myung Soon Kim and **Youn Soo Sohn***

Korea Institute of Science and Technology, Seoul, Korea

(Received Oct. 8, 1975)

요 약. 사면체 구조를 갖는 철(III)-옥살산 착화합물 5개와 팔면체 구조를 갖는 착화합물 3개를 합성한 후 화학분석과 적외선스펙트럼을 이용하여 이들 착이온의 구조에 관하여 연구하였다. 이들중 [FeC₂O₄Br₂]⁻, [FeC₂O₄(NCS)₄]³⁻ 및 [Fe₂(C₂O₄)₃Cl₄]⁴⁻ 등의 3개의 피리딘염은 아직 보고되지 않은 새로운 착물이며, 특히 이합체로 생각되는 착물 (PyH)₄[Fe₂(C₂O₄)₃Cl₄] 는 광화학 반응성이 아주 큼을 알 수 있었다. 이들 여러 철(III)-옥살산 착물의 몰전기전도도와 자기화율에 관한 측정결과와도 함께 보고하였다.

ABSTRACT. Amine salts of five tetrahedral and three octahedral oxalatoferrate(III) complexes have been prepared including pyridinium salts of unreported oxalate complex ions $[FeC_2O_4Br_2]^-$, $[FeC_2O_4(NCS)_4]^{3-}$ and $[Fe_2(C_2O_4)_3Cl_4]^{4-}$, the latter being most photoreactive. The structural aspects of these new complex ions as well as of other oxalatoferrates(III) have been discussed based on their analytical data and infrared spectra. The results of molar conductivity and magnetic susceptibility measurements of all these oxalatoferrate(III) complexes were also presented.

INTRODUCTION

In contrast to the trisoxalatoiron(III) complex which has been subjected to extensive studies[1~3] because of its photochemical interests[4,5], the mono- and dioxalatoferrate(III) complexes have little been studied. Although several mono- and dioxalatoferrate(III) complexes were early isolated in solid state by Weinland and Sierp[6] and their formation was confirmed also in solution[7~9], their molecular structure and properties are not fully characterized. To a surprise nearly no progress has been made on their chemistry since early 1920.

In this work several four- and six-coordinate oxalatoferrate (III) complexes were prepared including a few unreported, in order to examine their structural and chemical properties. Most of these oxalatoferrate(III) complexes were also found to be photosensitive.

EXPERIMENTAL

Aqueous stock solutions containing 0.8 gram-atom of ferric ion per liter were prepared using

---

* To whom inquiry should be addressed.

each of reagent grade $FeCl_3 \cdot 6H_2O$(Baker), Fe-$(NO_3)_3 \cdot 9H_2O$ and $Fe_2(SO_4)_2 \cdot xH_2O$ (Chameleon) and chemical pure ferric bromide aqueous solution (60%) (Mitsuwa) which was used without further purification. Amines and all other chemicals including oxalic acid dihydrate are reagent grade unless specified.

Most of the oxalatoferrate(III) complexes prepared in the following are photosensitive and should be kept in the dark. Chemical analysis and all the physical measurements of these complexes were performed using freshly prepared samples.

Chemical Analysis

An adequate amount of the sample (0.5~1.0 g) was accurately weighed for dissolution in 30 ml of distilled water in beaker. Ferric hydroxide was precipitated at pH=9~10 and separated by filtration. The ppt was used for the determination of iron(III) by red-ox titration[10], and the filtrate for the determinations of the anions ($C_2O_4^{2-}$, Cl^-, Br^-, SCN^- and/or SO_4^{2-}). The oxalate ion in the presence of chloride was determined directly by titration with permanganate in acid medium while in the presence of Br^- or SCN^- the removal of the latter as silver salt was necessary before titration. The analysis of halides or thiocyanate ion was performed by argentimetry. Sulfate ion was precipitated by adding excess barium chloride, which was back-titrated with EDTA.

Preparation of Tetrahedral Fe(III)-Oxalate Complexes

C_5H_5NH-, $(CH_3)_4N-$, and $(C_2H_5)_3NH[FeC_2O_4 \cdot Cl_2]$. 2.5 g of $H_2C_2O_4 \cdot 2H_2O$ (0.02 mole) was dissolved directly in 25 ml of ferric chloride stock solution (0.02 mole) and 0.04 mole of amine chloride was added. The resultant solution was subjected to slow evaporation until yellow-green crystals were formed, which were separated from the solution by decantation and

then washed twice each with cold water and methanol.

Chemical analysis. $C_5H_5NH[FeC_2O_4Cl_2]$: Found(%): Fe, 18.7; C_2O_4, 30.1; Cl, 23.3; C, 28.1; H, 2.05; N, 5.21. Calcd. (%): Fe, 18.9; C_2O_4, 29.8; Cl, 24.0; C, 28.5; H, 2.05; N, 4.95. $(CH_3)_4N[FeC_2O_4Cl_2]$: Found(%): Fe, 19.1; C_2O_4, 30.2; Cl, 24.0. Calcd. (%): Fe, 19.3; C_2O_4, 30.5; Cl, 24.5. $(C_2H_5)_3NH[FeC_2O_4Cl_2]$:Found(%): Fe, 17.2; C_2O_4, 27.1; Cl, 21.8. Calcd. (%): Fe, 17.6; C_2O_4, 27.8; Cl, 22.4.

$C_5H_5NH[FeC_2O_4Br_2]$. Oxalic acid(0.02 mole) was dissolved in 30 ml aqueous solution containing the equimolar amount of ferric bromide and then 0.04 moles of pyridine and HBr were added. The final solution was slowly evaporated at room temperature and a red crystalline compound was yielded.

Chemical analysis. Found(%): Fe, 14.2; C_2O_4, 21.6; Br, 41.9. Calcd. (%): Fe, 14.6; C_2O_4, 22.9; Br, 41.6.

$C_5H_5NH[FeC_2O_4SO_4] \cdot 2H_2O$. Oxalic acid(0.02 mole) was dissolved in 25 ml of ferric sulfate stock solution and to this solution 0.04 mole of pyridinium sulfate (3.2 ml pyridine plus 2.3 ml conc. H_2SO_4) was added. Slow evaporation of the resultant solution at ambient temperature lead to the formation of a green-yellow compound, which was cautiously washed with cold water and methanol.

Chemical analysis. Found(%): Fe, 16.3; C_2O_4, 24.9; SO_4, 27.4. Calcd. (%): Fe, 15.7; C_2O_4, 24.7; SO_4, 27.0.

Preparation of Octahedral Fe(III)-Oxalate Complexes

$C_5H_5NH[Fe(C_2O_4)_2(H_2O)_2]$. In 25 ml of stock solution of ferric chloride, bromide or nitrate (0.02 mole) or of ferric sulfate(0.01 mole) 5 g of oxalic acid was dissolved and then 3.2 ml of pyridine was added. Slow evaporation yielded

green crystals.

Chemical analysis. Found(%): Fe, 16.5; C_2O_4, 49.3. Calcd(%): Fe, 16.1; C_2O_4, 50.7. Increased mole ratios of oxalic acid and/or pyridine to Fe(III) resulted in the same composition.

$(C_5H_5NH)_3[Fe(C_2O_4)(NCS)_4]$. Ammonium thiocyanate(0.04 mole) was dissolved in the aqueous solution containing 0.02 mole of ferric ion, $0.02\sim0.06$ mole of oxalic acid and $0.02\sim$ 0.06 mole of pyridine. Slow evaporation of the deep red solution resulted in a dark red crystalline compound. The same compound could be obtained from the solution containing one mole of $C_5H_5NH[FeC_2O_4Cl_2]$ and 4 mole of NH_4SCN.

Chemical analysis. Found(%): Fe, 9.46; C_2O_4, 14.7; SCN, 37.3. Calcd. (%): Fe, 9.06; C_2O_4, 14.3; SCN, 37.7.

$(C_5H_5NH)_4[Fe_2(C_2O_4)_3Cl_4]$. Ferric chloride (0.02 mole) and oxalic acid (0.04 mole) are dissolved in 25 m*l* of methanol and then $0.04\sim$ 0.06 mole of pyridine was added. On standing overnight brown-yellow crystals were formed. Increased mole ratios of oxalic acid to ferric ion resulted in the same composition.

Chemical analysis. Found(%): Fe, 13.1; C_2O_4, 31.5; Cl, 16.2; C, 36.7; H, 3.04; N, 6.63. Calcd. (%): Fe, 13.3; C_2O_4, 31.5; Cl, 16.9; C, 37.1; H, 2.89; N, 6.69.

Physical Measurements.

The infrared spectra of the oxalatoferrate(III) complexes were recorded in KBr wafer by Beckman IR-12 Spectrophotometer. Conductivity measurements both in water and methanol were performed at 25 °C by means of Beckman Model RC-18 Conductivity Bridge. The magnetic susceptibility of the solid complexes was measured at 20 °C by Faraday method using Varian Model V-4000 electromagnet and Cahn RG electrobalance. In order to check ferromagnetic impurity in the samples the measurements were

carried out at two different field strengths (8 and 12 K gauss). Highly pure Hg [CO(CNS)$_4$] and $[Ni(en)_3]S_2O_3$ were employed as standard paramagnetic substance. The effective magnetic moment was calculated according to the formula $\mu_{eff}=2.828\sqrt{\chi_M T}$ where χ_M is molar susceptibility corrected for diamagnetism.

RESULTS and DISCUSSION

Synthesis. The general synthetic scheme attempted in this work for the preparation of tetrahedral oxalatoferrate(III) complexes is represented by the following equation.

$$FeX_3 + H_2C_2O_4 + RX \xrightarrow{\text{H}_2\text{O or MeOH}} R[FeC_2O_4X_2]$$
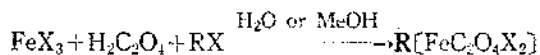
where X stands for Cl^-, Br^-, $\frac{1}{2}SO_4^{-2}$ and R for $C_5H_5NH^+$, $(C_2H_5)_3NH^+$, $(CH_3)_4N^+$. The experimental results show that the anion of the ferric salt need not be the same as that of the amine salt. For instance, if a chloride salt of amine is employed, only the dihalooxalatoferrate-(III) complex is always obtained whether or not the ferric salt is sulfate, nitrate, bromide or hydroxide. Such a result certainly indicates that the chloride ion is the better ligand as expected than any of these attempted.

The increased mole ratios of oxalic acid and/or amine salt to ferric ion also resulted in the same composition of the tetrahedral complex except for the case in which pyridinium salt was used. Pyridinium salt yielded in the aqueous solution the tetrahedral complex only at the equimolar ratio of oxalic acid and iron(III), but at the higher mole ratio, that is, [Ox]/ [Fe]$=2\sim3$ an octahedral diaquodioxalatoferrate-(III) complex was obtained.

Also the same tetrahedral complex was formed from the methanol solution containing ferric chloride and oxalic acid in the presense of triethylamine or tetramethylammonium chloride.

However in the presense of pyridine ferric chloride and oxalic acid in methanol produced completely a new different complex which might be tentatively formulated into an oxalate-bridged dinuclear form $(C_5H_5NH)_4[Fe_2(C_2O_4)_3Cl_4]$ with an octahedral local geometry of iron(III). Such an anomalous behavior of pyridine is not simply understood.

Another new crystalline complex tetrathiocy-anatooxalatoferrate(III) which is probably an octahedral form was isolated simply by conden-ation of the aqueous solution containing ferric

ion, oxalic acid, pyridine and excess thiocyanate ion. Only the same tetrathiocyanato complex was obtained regardless of their mole ratios. The same complex could also be produced from reaction of the tetrahedral dihalooxalatoferrate-(III) and excess thiocyanate ion.

The above-mentioned complexes mostly dis-solve in water and alcohols with partial decom-position but are insoluble in other organic solvents. Most of these complexes have been found to undergo photodecomposition in the daylight. In particular the dimer $(C_5H_5NH)_4$-
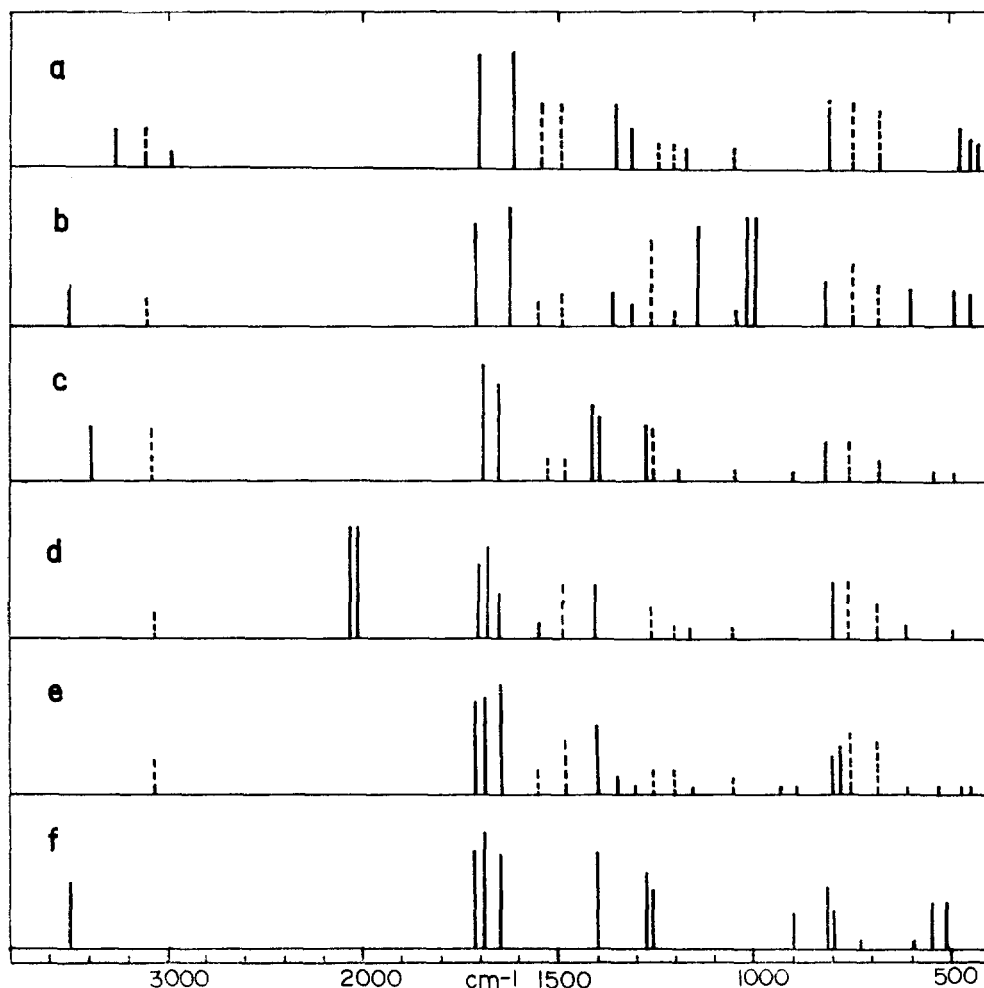

Fig. 1. IR spectra of a, $PyH[FeC_2O_4Cl_2]$; b, $PyH[FeC_2O_4SO_4] \cdot 2H_2O$; c, $PyH[Fe(C_2O_4)_2(H_2O)_2]$; d, $(PyH)_3[FeC_2O_4(NCS)_4]$; e, $(PyH)_4[Fe_2(C_2O_4)_3Cl_4]$; f, $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$.

$[Fe_2(C_2O_4)_3Cl_4]$ is most photosensitive while $(C_5H_5NH)[Fe(C_2O_4)_2(H_2O)_2]$ least photosensitive.

In the preceding section all the oxalatoferrate-(III) complex ions prepared in this work have already been classified into tetrahedral or octahedral structure with no conferred reasoning, which will be discussed below. The complex ions such as dihalooxaltoferrates(III) are obvious for their tetrahedral structure from their analytical data and coordination numbers derived therefrom. However, in other cases further informations, for example, cryoscopic and IR data would be required for exact structural formulation. A suitable solvent however could hardly be found for their cryoscopic measurements, but their IR spectra along with the results of molar conductivity and magnetic susceptibility measurements were mostly enough for elucidation on the nature of their coordination.

IR Spectra. The IR spectra of the pyridinium salts of the oxalatoferrate(III) complexes are exhibited in *Fig.* 1 including the well known spectrum of potassium trisoxalatoferrate(III)[11,12] as reference for the purpose of comparison. The bands originated from the pyridinium ion could easily be distinguished out(dotted lines) in each of those complex spectra. Then the remaining bands mostly originated from the complex ions may easily be corresponded to each of the frequencies of the trisoxalatoferrate-(III) which have already been assigned and new bands from the ligand vibrations other than oxalate ion can be identified.

It is generally seen in the figure that the vibrational modes $\nu(Fe-O)$ and $\delta(O-C=O)$ at 530 and 505cm^{-1} respectively in the trisoxalatoferrate(III) are observed at lower frequencies in the tetrahedral complexes and only very weakly observed in other complexes. Also the bands at 890, 1270 and 1390 cm^{-1} which arise predomin-

antly from C—O stretching vibrations in the reference compound are partly or completely disappeared in the complexes with mixed ligands while the ring deformation modes $\delta(O-C=O)$ around 800 cm^{-1} appears in all cases.

The most striking spectral feature however is the observed different patterns of carbonyl stretching vibration $(C=O)$ in these various complexes, since such patterns reflect sharply the structural differences among these complexes. The detailed spectra of the carbonyl stretching
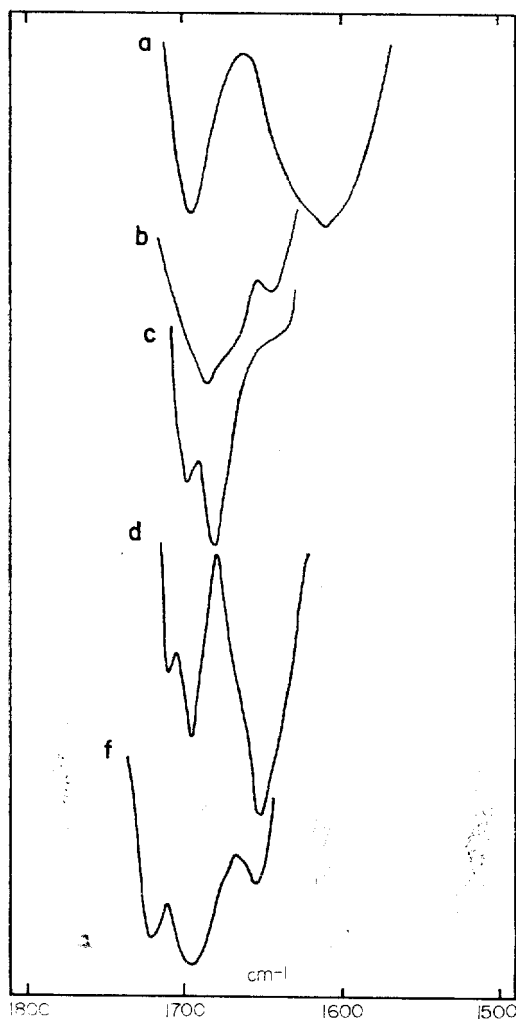

Fig. 2. Carbonyl stretching bands of a, $[FeC_2O_4Cl_2]^-$; b, $[Fe(C_2O_4)_2(H_2O)_2]^-$; c, $[FeC_2O_4(NCS)_4]^{3-}$; d, $[Fe_2(C_2O_4)_3Cl_4]^{4-}$; e, $[Fe(C_2O_4)_3]^{3-}$.

region are therefore reproduced in *Fig.* 2. Each of the complex ions having oxalate ion as ligand shows its characterestics in the band shape and position which have been found to be independent of its cations. It is seen in the figure that generally three different carbonyl stretching frequencies are observed in the highly distorted octahedral complex ions regardless of the numbers of the oxalato-ligand whereas only two in the tetrahedral complex involving only one oxalate ligand, which is in accord with the theoretically predicted. The observation of only two carbonyl bands however in $[Fe(C_2O_4)_2(H_2O)_2]^-$ which is probably also a distorted octahedral form indicates that the aquo ligands are in trans position so as to retain higher molecular symmetry $(D_{4h}$ or $D_{2h})$.

One of the most conclusive evidences for the sulfato complex being a tetrahedral form, that is, $PyH[FeC_2O_4SO_4]\cdot 2H_2O$ instead of an octahedral $PyH[FeC_2O_4SO_4(H_2O)_2]$ comes also from the observation of the exactly same pattern of the C=O stretching bands as that of the dichlorooxalatoferrate(III) complex as shown in *Fig.* 1. The two spectra of $PyH[FeC_2O_4Cl_2]$ and $PyH[FeC_2O_4SO_4]\cdot 2H_2O$ are shown to be closely resembled also in other region, if the strong absorptions by sulfate ion at 600, 990, 1010, 1130 and 1250 cm^{-1}(overlapped by a pyridinium ion band) are exempted. In fact, such a vibrational pattern of the sulfate ion is indicative of its chelated structure.[13] Another evidence for the water molecules in the sulfato complex to be crystal water instead of coordinated one is seen from the high O—H stretching frequency at 3500 cm^{-1} which is exactly the same as that of the hydrated water in the reference compound. On the other hand the O—H vibration in $PyH[Fe(C_2O_4)_2(H_2O)_2]$ is observed at remarkably lower frequency (3400 cm^{-1}) and as such shows the water molecules to be coordinated.

In general the thiocyanate group in a metal complex may coordinate to the metal through the nitrogen or the sulfur. The observation of the CN stretching vibrations at low frequencies (2040 and 2065 cm^{-1})[14] in the thiocyanato complex evidently indicates the N-coordination in this case and consequently its correct formula should be written in the form of isothiocyanate complex $(PyH)_3[FeC_2O_4(NCS)_4]$.

Another interesting point is the IR spectrum of the new dinuclear complex $(PyH)_4[Fe_2(C_2O_4)_3Cl_4]$. As a matter of fact no definitive evidence for the dimeric structure is directly available from its IR spectrum. However all other possibilities for the complex ion to be any adduct form of $PyH[FeCl_4]\cdot(PyH)_3[Fe(C_2O_4)_3]$, $PyH[FeC_2O_4Cl_2]\cdot(PyH)_3[Fe(C_2O_4)_2Cl_2]$ or $4PyHCl\cdot Fe_2(C_2O_4)_3$ could be clearly excluded simply by comparing the IR spectra of adduct components with that of the complex which shows uniqueness particularly of its carbonyl stretching band. Further study on its molecular structure and other interesting properties are underway.

Molar Conductivity. In order to examine the behavior of the oxalatoferrate(III) complexes in solution their molar conductivity has been measured in water and methanol and the results are given in *Table* 1. Tetramethylammonium chloride would obviously dissociate into two monovalent ions both in water and methanol. It is reasonable to assume no significant differ-

Table 1. Results of molar conductivity measurements.

Compounds	Molar conductivity, ohm^{-1} cm^{-1}	
	in H_2O	in MeOH
$(CH_3)_4NCl$	1.09×10^2	1.08×10^2
$(CH_3)_4N[FeC_2O_4Cl_2]$	2.57×10^2	1.19×10^2
$C_5H_5NH[FeC_2O_4Cl_2]$	2.57×10^2	1.09×10^2
$C_5H_5NH[Fe C_2O_4Br_2]$	2.72×10^2	1.59×10^2
$C_5H_5NH[Fe(C_2O_4)_2(H_2O)_2]$	0.87×10^2	—
$(C_5H_5NH)_4[Fe_2(C_2O_4)_3Cl_4]$	5.09×10^2	3.07×10^2

ence between the mobilities of $(CH_3)_4N^+$ and PyH^+, since the molar conductivities of the two different salts with the same complex anion are measured to be the same. By comparing the molar conductivity of $PyH[Fe(C_2O_4)_2(H_2O)_2]$ with that of $(CH_3)_4NCl$, it may also be assumed that the ionic mobilities of the complex anions are not remarkably lower than that of chloride ion.

Under such assumptions the results of molar conductivity measurements indicate that the tetrahedral dihalooxalatoferrate(III) ion undergoes no dissociation in methanol but partially dissociate in water probably with elimination of the chloride ions from the coordination sphere. Also partial dissociation seems to take place in the dinuclear complex ion in water but only ionization in methanol.

Magnetic Susceptibility. In *Table* 2 the results of the magnetic susceptility measurements of the oxalatoferrate(III) complexes prepared in this work are given along with those of some other tetrahedral iron(III) complexes not included in this study. The results show that all the tetrahedral oxalatoferrate(III) complexes exhibit lower magnetic moments while the values of the octahedral complexes are proximate to the

psin-only value 5.92 B. M.

Although many of the iron(III) complexes are known to show very complicated magnetic behavior,[15] it is a striking aspect that all the tetrahedral complexes involving oxalate ion as ligand show such lower magnetic moment than the spin-only value. Some other tetrahedral iron(III) complexes showing lower magnetic moment could be sought in the literature.[16] Therefore, it can be envisioned that many of the tetrahedral iron(III) complexes may be not magnetically dilute even if the mechanism can hardly be explicable at the present time. In order to confirm and elucidate the antiferromagnetism associated with these systems further studies including temperature-dependent measurements should be carried out.

REFERENCES

1. A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer and R. D. Lindholm, *Chem. Res.*, **68**, 541 (1968) and references therein.
2. G. G. Savelyev, A. A. Medvinskii, V. L. Shtsherinskii, L. P. Gevlitch, N. I. Gavryusheva, Yu. T. Pavlyukhin and L. L. Stepapanova, *J. Solid State Chem.*, **12**, 92 (1975) and references therein.
3. W. M. Riggs, *J. Inorg. Nucl. Chem.*, **33**, 1635 (1971).
4. H. E. Spencer and M. W. Schmidt, *J. Phys. Chem.*, **75**, 2986 (1971).
5. D. Callaby and M. Brotto, *J. Photogr. Science.*, **18**, 8 (1970).
6. R. F. Weinland and F. W. Sierp, *Z. anorg. Chem.*, **117**, 59 (1921).
7. M. Bobtesky, D. Chasson and S. F. Klein, *Anal. Chim. Acta.*, **8**, 460 (1953).
8. A. K. Babko and L. I. Dubovenko, *Zhur. Obshchei Khim.*, **26**, 660 (1956).
9. A. Yamada, *Nippon Kaagaku Zaschi*, **84**, 224 (1963).
10. I. M. Kolthoff, E. B. Sandell, E. J. Meehan and S. Bruckenstein, "Quant. Chem. Anal.," 4th Ed. P. 839, Mcmillan Co., London, 1969.

Table 2. Results of magnetic moment measurements.

Compounds	μ_{eff}(B. M.)
$(CH_3)_4N[FeC_2O_4Cl_2]$	5.33
$C_5H_5NH[FeC_2O_4Cl_2]$	5.30
$C_5H_5NH[FeC_2O_4Br_2]$	5.34
$C_5H_5NH[FeC_2O_4SO_4] \cdot 2H_2O$	5.36
$C_5H_5NH[Fe(C_2O_4)_2(H_2O)_2]$	5.85
$(C_5H_5NH)_3[FeC_2O_4(NCS)_4]$	5.94
$(C_5H_5NH)_4[Fe_2(C_2O_4)_3Cl_4]$	5.59**
$C_5H_5NH[FeC_2O_4SO_4]^*$	5.1
$[Fe(HCOO)_2]\ Cl \cdot H_2O^*$	5.3
$NH_4[Fe(SO_4)_2]^*$	5.6
$(NH_4)_3[Fe(PO_4)_2]^*$	5.7

*Ref. 16; ** per iron (III).

崔奇珠·金明淳·孫蓮秀

11. K. Nakamoto, "IR Spectra of Inorg. and Coord. Compds." 2nd Ed., P. 245, Wiley-Interscience, New York, 1970.

12. J. Fujita, A. E. Martell and K. Nakamoto, *J. Chem. Phys.*, **36**, 324, 331 (1962).

13. R. Eskenazi, J. Raskovan, and R. Levitus, *J. Inorg. Nucl. Chem.*, **28**, 521 (1966).

14. P. C. H. Mitchel and R. J. P. Williams. *J. Chem. Soc.*, 1912 (1960).

15. B. N. Figgis and J. Lewis, The Mag. Prop. of Trans. Metal Complexes, "Progress in Inorg. Chem", Vol. 6, P. 37, Interscience, New York, 1964.

16. L. A. Welo, *Phil. Mag.*, **6**, 481 (1928).