Inorganica Chimica Acta, 124 (1986) 49–53

Magnetic Circular Dichroism of Tetrahedral Complexes of Iron(III)

TSUGUFUMI MURAOKA

School of Education, Miyazaki University, Miyazaki 880, Japan

TSUNENORI NOZAWA and MASAHIRO HATANO

Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Sendai 980, Japan

Received November 14, 1985

Abstract

The magnetic circular dichroism spectra for the spin-forbidden d–d transitions of FeX_4 (X = Cl and Br) were obtained and revealed to have large Faraday *C* term contribution. Comparison of the MCD results with those of previously proposed theoretical ones clarified the electronic origins and revealed that the first and second spin-forbidden bands are due to the $^4T_1(G) \leftarrow {}^6A_1$ transitions. The MCD analysis for bis(*o*-xylyl-α,α′-dithiolato)ferrate(III) ion indicated that the transitions around 15 000 cm^{-1} consist of at least two components, $^4T_1(G) \leftarrow {}^6A_1$ and $^4T_2(G) \leftarrow {}^6A_1$.

Introduction

In recent years, iron sulfur complexes have been extensively investigated as models for iron sulfur proteins [1–5]. Lane and co-workers prepared bis(*o*-xylyl-α,α′-dithiolato)ferrate(III) anion ($[Fe(S_2\text{-}o\text{-}xyl)_2]^-$) as a model for oxidized rubredoxin which has one iron tetrahedral core structure [6]. A recent fluorescence X-ray absorption and X-ray analysis show that the geometry around the iron(III) core in the oxidized rubredoxin is nearly tetrahedral [7, 8]. Eaton and co-workers measured the near infrared (near IR) spectra for oxidized and reduced rubredoxin, and found several low intensity absorption bands [9]. One of the bands in the near IR region for oxidized rubredoxin, *i.e.*, the peak at 13 400 cm^{-1}, had been assigned to the sulfur → iron charge-transfer transition, by comparison of circular dichroism (CD) with absorption spectra. Later this assignment was revised to the spin-forbidden d–d transition, based on the energy separation between ^6S–^4G for the free iron(III) ion [10]. On the other hand, the energy levels for the tetrahedral $Fe(III)S_4$ core, calculated by using an *ab initio* molecular orbital theory [11] or ligand field parameters [12], revealed that the bands below 17 000 cm^{-1} were attributable to the components of spin-forbidden transitions. Thus, the assignment of this band remains uncertain for lack of conclusive evidence.

Tetrahalogeno complexes, $[FeX_4]^-$, seem to have the same tetrahedral symmetry around the iron atom as that of rubredoxin or the $[Fe(S_2\text{-}o\text{-}xyl)_2]^-$ ion, which has been well characterized crystallographically [3]. Lauer and Ibers have indicated that the $[FeCl_4]^-$ ion has a slightly distorted tetrahedral structure from X-ray analysis [13]. The electronic transitions for these complexes have been studied independently by many investigators [14–20]. Although several assignments have been proposed based on many experimental techniques, the assignments have not yet been established.

Magnetic circular dichroism (MCD) spectroscopy is a powerful technique for exploring the electronic structures for metal complexes and organic molecules [21–24]. Rivoal and co-workers have measured the MCD spectra for the tetrahedral iron(III) complexes, such as $[FeCl_4]^-$, $[FeBr_4]^-$ and oxidized rubredoxin, and have provided significant information on the assignments of the charge-transfer transitions [25, 26]. The $[MnX_4]^{2-}$ ions with the same d^5 configuration as that of $[FeX_4]^-$ ions were studied by the MCD, and MCD signs observed experimentallly showed fundamental agreement with those predicted theoretically [27–29].

We have reported previously that the $[Fe(S_2\text{-}o\text{-}xyl)_2]^-$ ion gives an MCD spectrum which closely resembles that of rubredoxin, although no spectroscopic assignment of the lowest energy bands was discussed [30]. We present here the MCD spectra for the spin-forbidden d–d transition bands of tetrahedral ferric complexes, and discuss the assignments of $[FeX_4]^-$ (X = Cl and Br) ions based on the MCD analysis. Furthermore, the MCD bands of the lower transitions for the $[Fe(S_2\text{-}o\text{-}xyl)_2]^-$ ion are characterized in this paper.

Experimental

$(Et_4N)[FeX_4]$ (X = Cl and Br) and $(Et_4N)[Fe(S_2\text{-}o\text{-}xyl)_2]$ were prepared according to the method of

0020-1693/86/$3.50

Gill [31] and Lane *et al.* [3], respectively. MCD spectra were recorded on a JASCO J20A circular dichroism spectrometer using a JASCO electromagnet with 1.14 T at the sample. Electronic absorption spectra were measured with Hitachi model EPS-3T and model 200-10 spectrophotometer. The values of molar extinction coefficients ϵ in absorption spectra and magnetic molar ellipticities $[\theta]_M$ in MCD were in unit of dm^3 mol^{-1} cm^{-1} and deg dm^3 mol^{-1} cm^{-1} $gauss^{-1}$, respectively.

Results and Discussion

The Tanabe–Sugano energy diagram [32] predicts that the low intensity transition observed in the region 10 000–23 000 cm^{-1} is $^6\Gamma \leftarrow {}^4A_1$ or $^2\Gamma \leftarrow {}^6A_1$ in tetrahedral symmetry, which we took as a first approximation in this paper. The above prediction is consistent with the following assignments in that these bands are derived from spin-forbidden transitions. Because the transition $^2\Gamma \leftarrow {}^6A_1$ can gain intensity only at very low temperature [16], and no new bands appeared in the electronic absorption spectra with a decrease of temperature to 220 K, the $^2\Gamma \leftarrow {}^6A_1$ transition can be neglected in the following treatment. Since the magnitude of the MCD band increases in proportion to the reciprocals of the absolute temperature with little change in intensity of the absorption band, the MCD bands in this region are ascribable to 'so-called' Faraday *C* terms. Ligand field theory, including the spin–orbit interaction, tells us that the Faraday *C* terms are predominant for the transition $^4\Gamma \leftarrow {}^6A_1$ [28]. Only the $^4A_1 \leftarrow {}^6A_1$ transition gives no Faraday *C* term because there is no transition moment even after inclusion of the spin–orbit interaction.

[FeCl$_4$]$^-$ and [FeBr$_4$]$^-$ Ions

Although the absorption spectra of $[FeCl_4]^-$ ion have been studied by many investigators, several unresolved problems remain, mainly in the assignment of the spin-forbidden transitions. This problem is due to the following two factors: (1) the bands for respective multiplets overlap with each other, and (2) the band splittings in respective multiplets are very large. To overcome these difficulties, low temperature polarized spectra have recently been applied and provided some important information to settle the assignments [18]. The MCD technique is anticipated to give further insight because of better resolution, owing to the fact that the MCD spectra can be either positive or negative in sign for respective multiplets. Vala and co-workers have calculated the Faraday *C* terms for the tetrahedral d^5 configuration with a crystal field approximation including spin–orbit interactions [28]. Table I gives their results.

TABLE I. C/D^a for $^4\Gamma \leftarrow {}^6A_1$ Transitions Calculated by Vala *et al.* [28]

$^4\Gamma$	$^4A_1$	$^4A_2$	^4E	$^4T_1$	$^4T_2$
C/D		−7	+7/2	+7/2	−7/2

[a] A positive *C/D* gives negative MCD, where *C* and *D* are Faraday *C* term and dipole strength in unit of reduced matrix elements.

The Tanabe–Sugano energy diagram predicts that the lowest spin-forbidden d–d transition is assigned to $^4T_1(G) \leftarrow {}^6A_1$, which theoretically gives a negative MCD. The observed sign of the first MCD band is consistent with the theoretical one. However, the second MCD band around 14 600 cm^{-1} shows a sign different from the theoretical prediction, because the MCD for the next higher $^4T_2(G) \leftarrow {}^6A_1$ transition is positive, as shown in Table I. The second band has been variously assigned as the transition to $^4T_1(G)$ or $^4T_2(G)$ of the spin–orbit component of $^4T_1(G)$ [14–20]. The energy difference between the first and second MCD band is 600 cm^{-1}, which is too large to attribute to the spin–orbit splittings, because they have been estimated to be 260 cm^{-1} by Vala and McCarthy [18]. The energy difference between $^4T_1(G)$ and the next higher $^4T_1(G)$ states is estimated to be *ca.* 3000 cm^{-1} [32], which is too large relative to the observed one. Therefore, we assign both of the negative MCD bands to $^4T_1(G) \leftarrow {}^6A_1$ transitions, while the positive MCD observed in the region 16 000 to 17 000 cm^{-1} is assigned to the $^4T_2(G) \leftarrow {}^6A_1$ transition.

The absorption spectrum in the region 17 000 to 20 000 cm^{-1} gives a rather sharp band with no band splitting. The narrow width of the absorption band is known to be derived from the transition to the field independent state, because the energy level is independent of small variations of the ligand field associated with molecular vibrations [32]. Jϕrgensen *et al.* have assigned this band to $^4E(G) \leftarrow {}^6A_1$, because only the $^4E(G)$ and $^4E(D)$ states are independent of the ligand field [16a]. However, it is difficult to assign the band around 18 800 cm^{-1} to the transition to $^4E(G)$ or $^4E(D)$, because the negative MCD expected theoretically is not found in this region. Balt has pointed out that according to ligand field theory, including the spin–orbit interaction, the dipole strength is large for $^4E(D) \leftarrow {}^6A_1$ but rather small for $^4E(G) \leftarrow {}^6A_1$ transition [16b]. Since the small MCD with the negative sign which originated from the $^4E(G) \leftarrow {}^6A_1$ transition seems to be buried in large MCD of positive sign in the vicinity, the positive MCD band around 18 800 cm^{-1} could be assigned to the transition to $^4T_2(D)$, which is the higher energy state next to $^4E(D)$.

Around 22 000 cm^{-1}, a couple of positive and negative MCD are observed. The energy diagram indicates that the negative MCD is derived from the transition to $^4E(D)$ or $^4T_1(P)$, but no positive sign of the MCD is expected theoretically. Therefore, we assign the negative MCD band to the transition to the $^4E(D)$ state, which is the next higher energy level above $^4T_2(D)$. The positive band at 21 900 cm^{-1} seems to arise from overlap of the negative MCD at 22 400 cm^{-1} with a major charge-transfer band with a positive sign.

The MCD spectrum for the $[FeBr_4]^-$ ion demonstrates an MCD spectral feature with similar signs to that of the $[FeCl_4]^-$ ion. Differences between them exist only in the region of the higher wave numbers. These differences may be attributed to the effect of the close proximity of the charge-transfer bands. Except for this region, the MCD spectrum of the $[FeBr_4]^-$ ion indicates that this ion should have energy states similar to those of the $[FeCl_4]^-$ ion. Table II gives the plausible assignment of the bands for the $[FeBr_4]^-$ ion from the comparison with that for $[FeCl_4]^-$ ion, together with an indication of the Vala–McCarthy energy diagram and assignment [19].

TABLE II. Observed MCD Signs and their Possible Assignments for $[FeBr_4]^-$ and $[FeBr_4]^-$ Ions.

$[FeCl_4]^-$ (Fig. 1)		$[FeBr_4]^-$ (Fig. 2)	
Observed MCD $\tilde{\nu} \times 10^{-3}$ (cm^{-1})	Assignment	Observed MCD $\tilde{\nu} \times 10^{-3}$ (cm^{-1})	Assignment
−14.0	$^4T_1(G)$	−11.9	$^4T_1(G)$
−14.6		−12.8	
+16.7	$^4T_2(G)$	+13.5	$^4T_2(G)$
		+14.1	
		+14.4	
+18.8	$^4T_2(D)$	+15.7	$^4T_2(D)$
+19.0			
+21.9			
−22.4	$^4E(D)$	−16.0	$^4E(D)$
		+16.2	
		−16.4	$^4T_1(P)$

$[Fe(S_2\text{-}o\text{-}xyl)_2]^-$ Ion

Figure 3 shows the MCD and absorption spectra for the $[Fe(S_2\text{-}o\text{-}xyl)_2]^-$ ion. The absorption spectrum above 17 400 cm^{-1} has been assigned to the charge-transfer transitions because of the large extinction coefficients and high transition energies [3, 11, 33]. Although the characteristically broad band around 15 000 cm^{-1} has lower magnitude of absorp-

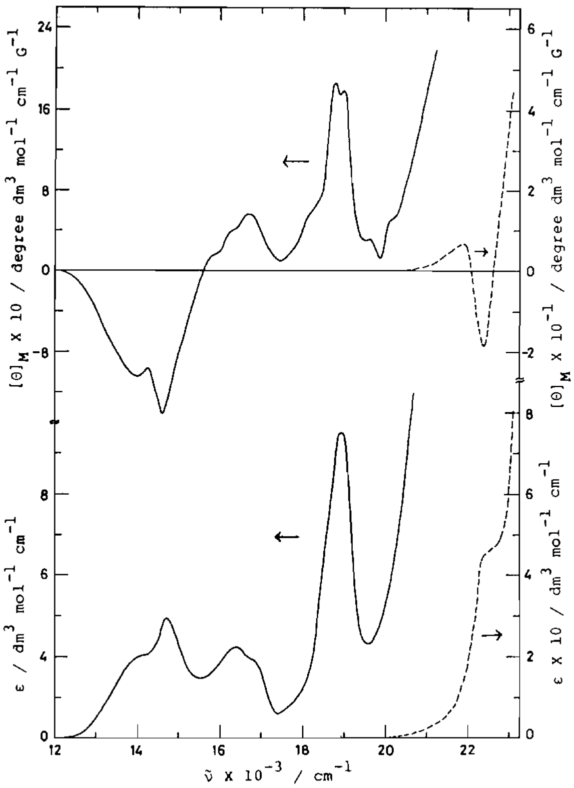

Fig. 1. MCD (upper) and absorption (lower) spectra for $(Et_4N)[FeCl_4]$ in dimethylformamide (DMF) solution containing 0.1 M $(C_2H_5)_4NCl$ at room temperature.

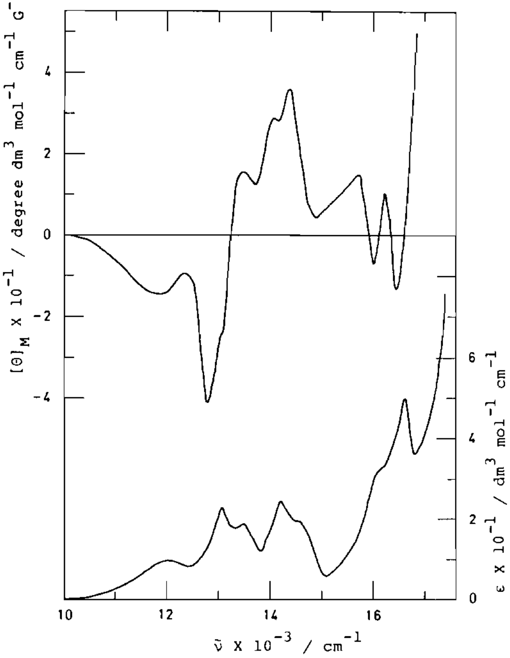

Fig. 2. MCD (upper) and absorption (lower) spectra for $(Et_4N)[FeBr_4]$ in DMF solution containing 0.1 M $(C_2H_5)_4NBr$ at room temperature.

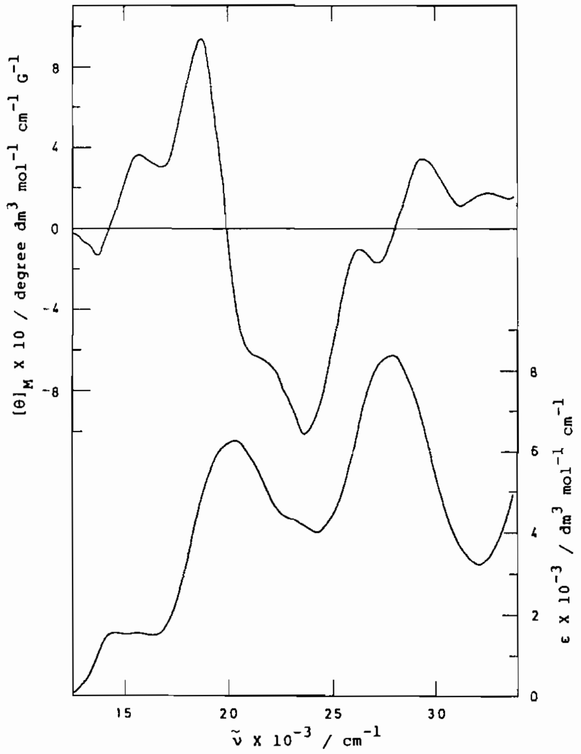

Fig. 3. MCD (upper) and absorption (lower) spectra for $(Et_4N)[Fe(S_2\text{-}o\text{-}xyl)_2]$ in DMF at room temperature.

tion than the other bands, the assignment of this band is uncertain because of the complexity of the band shape.

Figure 3 shows that the lowest MCD of the $[Fe(S_2\text{-}o\text{-}xyl)_2]^-$ ion gives a negative sign. This experimental result is in conflict with the assignment of the band around 15 000 cm^{-1} as a charge-transfer transition, since the MCD spectra for complexes with a tetrahedral iron(III) ion, such as $[FeCl_4]^-$, $[FeBr_4]^-$ and oxidized rubredoxin, are positive for the lowest energy band of the charge-transfer transition [10, 25, 26]. From these facts, we propose that the lowest energy band is probably attributable to the d–d transition for the iron(III) ion, $^4T_1(G) \leftarrow {}^6A_1$ or $^4E(D) \leftarrow {}^6A_1$, with a negative sign of MCD, as shown in Table I. Since the transition energy of this band seems too small to assign the band to $^4E \leftarrow {}^6A_1$ [32], we assign this band as the transition $^4T_1(G) \leftarrow {}^6A_1$. This assignment is consistent with the following theoretical considerations. The energy of the transition has been estimated to be about 13 500–15 000 cm^{-1} by Rawlings *et al.*, based on ligand field parameters such as $-10Dq = 6 \sim 8 \times 10^3$ cm^{-1}, $B = 600$ cm^{-1} and $C/D = 4.5$ [12]. From the calculation of molecular orbitals for the $Fe(III)S_4$ core, Bair and Goddard [11] have obtained a transition energy for the spin-forbidden band similar to that of Rawlings *et al.* On the basis of these facts, we assign the band with negative MCD around 13 500 cm^{-1} to the $^4T_1(G) \leftarrow {}^6A_1$ transition.

The MCD in the higher energy level next to the $^4T_1(G) \leftarrow {}^6A_1$ transition has a positive sign. Since the absorption band corresponding to this MCD is of the same magnitude as that of the $^4T_1(G) \leftarrow {}^6A_1$ transition, the second MCD band seems to be assigned to the d–d transition. The energy diagram indicates that the level next to the $^4T_1(G)$ is $^4T_2(G)$, which is located at about 2500 cm^{-1} in the higher energy side. Since the MCD of $^4T_2(G) \leftarrow {}^6A_1$ for the $[FeX_4]^-$ ion exhibited a positive sign, the most probable assignment of the band around 16 000 cm^{-1} might be the $^4T_2(G) \leftarrow {}^6A_1$ transition.

Conclusion

The MCD results of the tetrahedral iron(III) ion gave valuable information about spin-forbidden d–d transitions. The MCD bands for the $[FeX_4]^-$ ion assigned to $^4T_1(G) \leftarrow {}^6A_1$ and $^4T_2(G) \leftarrow {}^6A_1$ transitions showed negative and positive signs, respectively, which agreed with the theoretical prediction. The MCD analysis for the $[Fe(S_2\text{-}o\text{-}xyl)_2]^-$ ion leads us to conclude that the broad absorption bands around 15 000 cm^{-1} are attributable to the d–d transitions.

References

1 R. H. Holm, *Endeavour, 34,* 38 (1975).
2 R. H. Holm and J. A. Ibers, in W. Lovenberg (ed.), 'Iron–Sulfur Proteins', Vol. III, Academic Press, New York, 1977, Chap. 7, and refs. therein.
3 (a) R. W. Lane, J. A. Ibers, R. B. Frankel and R. H. Holm, *Proc. Nat. Acad. Sci. U.S.A., 7,* 2868 (1975); (b) R. W. Lane, J. A. Ibers, R. B. Frankel, G. C. Papaefthymiou and R. H. Holm, *J. Am. Chem. Soc., 99,* 84 (1977).
4 D. Coucouvanis, D. Swenson, N. C. Baenzinger, C. Murphy, D. G. Holah, N. Sfarnas, A. Simopoulos and A. Kostikas, *J. Am. Chem. Soc., 103,* 3350 (1981).
5 M. Millar, J. F. Lee, S. A. Koch and R. Fikar, *Inorg. Chem., 21,* 4106 (1982).
6 L. H. Jensene, in W. Lovenberg (ed.), 'Iron–Sulfur Proteins', Vol. II, Academic Press, New York, 1973, Chap. 4.
7 R. G. Shulman, P. Eisenberger, B. K. Teo, B. M. Kincaid and G. S. Brown, *J. Mol. Biol., 124,* 305 (1978).
8 (a) K. D. Watenpaugh, L. C. Sieker and L. H. Jensene, *J. Mol. Biol., 131,* 509 (1979); (b) K. D. Watenpaugh, L. C. Sieker and L. H. Jensene, *J. Mol. Biol., 138,* 615 (1980).
9 W. A. Eaton, G. Palmer, J. A. Fee, T. Kimura and W. Lovenberg, *Proc. Nat. Acad. Sci. U.S.A., 68,* 3015 (1971).
10 W. A. Eaton and W. Lovenberg, in W. Lovenberg (ed.), 'Iron–Sulfur Proteins', Vol. II, Academic Press, New York, 1973, Chap. 3.
11 (a) R. A. Bair and W. A. Goddard, III, *J. Am. Chem. Soc., 99,* 3505 (1977); (b) R. A. Bair and W. A. Goddard, III, *J. Am. Chem. Soc., 100,* 5669 (1978).
12 J. Rawlings, O. Siiman and H. B. Gray, *Proc. Nat. Acad. Sci. U.S.A., 71,* 125 (1974).

13 J. W. Lauher and J. A. Ibers, *Inorg. Chem.*, *14*, 348 (1975).

14 B. J. Hathaway and D. G. Holah, *J. Chem. Soc.*, 2408 (1964).

15 A. P. Ginsberg and M. B. Robin, *Inorg. Chem.*, *2*, 817 (1963).

16 (a) S. Balt, *Recl. Trav. Chim.*, *86*, 1024 (1967); (b) S. Balt, *Mol. Phys.*, *14*, 233 (1968).

17 T. J. Kistenmacher and G. D. Stucky, *Inorg. Chem.*, *7*, 2150 (1968).

18 M. A. Vala, Jr. and P. J. McCarthy, *Spectrochim. Acta, Part A*, *26*, 2183 (1970).

19 M. Vala, Jr., P. Mongan and P. J. McCarthy, *J. Chem. Soc., Dalton Trans.*, 1870 (1972).

20 N. Islam, *Appl. Spectrosc.*, *728*, 277 (1974).

21 P. J. Stephens, *Ann. Rev. Phys. Chem.*, *25*, 201 (1974).

22 P. Day (ed.), 'Electronic States of Inorganic Compounds: New Experimental Techniques', Reidel, Dordrecht, 1975.

23 E. W. Thulstrup, 'Linear and Magnetic Circular Dichroism of Planar Organic Molecules', Springer-Verlag, Berlin, 1980.

24 S. B. Piepho and P. N. Schatz, 'Group Theory in Spectroscopy with Application to Magnetic Circular Dichroism', Wiley-Interscience, New York, 1983.

25 J. C. Rivoal and B. Briat, *Mol. Phys.*, *27*, 1081 (1974).

26 J. C. Rivoal, B. Briat, R. Cammack, D. O. Hall, K. K. Rao, I. N. Douglas and A. J. Thomson, *Biochim. Biophys. Acta*, *493*, 122 (1977).

27 H. Kato, *J. Chem. Phys.*, *58*, 1964 (1973).

28 M. Vala, J. C. Rivoal and J. Badoz, *Mol. Phys.*, *30*, 1325 (1975).

29 J. C. Rivoal, B. Briat and M. Vala, *Mol. Phys.*, *38*, 1829 (1979).

30 (a) T. Muraoka, T. Nozawa and M. Hatano, *Chem. Lett.*, 1373 (1976); (b) T. Muraoka, T. Nozawa and M. Hatano, *Bioinorg. Chem.*, *8*, 45 (1978).

31 N. S. Gill, *J. Chem. Soc.*, 3512 (1961).

32 S. Sugano, Y. Tanabe and H. Kamimura, 'Multiplet of Transition Metal Ions in Crystals', Academic Press, New York, 1970.

33 J. V. Pivnichny and H. H. Brinzinger, *Inorg. Chem.*, *12*, 2839 (1973).