Inorg. Chem. **1983**, *22*, 993–995

effects have parallels in both electrochemical and NMR data, steric effects do not. The lack of correlation between carbon-13 and phosphorus-31 in other $Cr(CO)_5L$ complexes[69] is also consistent with these ideas.

Acknowledgment. This work was financially supported by the Australian Research Grants Committee.

Registry No. 1, 14911-72-9; **2**, 14911-71-8; **3**, 34818-93-4; **4**, 40545-00-4; **5**, 69021-33-6; **6**, 18461-32-0; **7**, 18461-33-1; **8**, 18461-39-7; **9**, 14917-12-5; **10**, 36491-08-4; **11**, 84051-19-4; **12**, 15228-38-3; **13**, 14740-77-3; **14**, 13007-92-6.

---

(69) J. Grobe and D. le Van, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, **34B**, 1653 (1979).

Contribution from the Departments of Chemistry,
The University of Texas, Austin, Texas 78712,
and University of Alabama, University, Alabama 35486

Synthesis and X-ray Crystal Structure of Tris(di-*tert*-butylphosphido)tricarbonyltrirhodium(I)

J. L. Atwood,*[1] W. E. Hunter,[1] R. A. Jones,*[2] and T. C. Wright[2]

Received May 24, 1982

As part of a program[3] to investigate steric and electronic effects in transition-metal phosphido (R_2P^-) and phosphinidene (RP^{2-}) complexes, we have studied the reaction of $[Rh(CO)_2Cl]_2$ with t-Bu_2PLi in tetrahydrofuran.[4] From this reaction we have isolated and characterized several dinuclear complexes[4] and also the rhodium(I) trimer $[Rh(\mu\text{-}t\text{-}Bu_2P)CO]_3$. We report here details of the isolation, characterization, and X-ray crystal structure of the trinuclear complex.

Experimental Section

All operations were performed under nitrogen or under vacuum. Microanalyses were by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Hexane and THF were dried over sodium and distilled from sodium/benzophenone under nitrogen before use. t-Bu_2PLi[5] and $[Rh(CO)_2Cl]_2$[6] were prepared by literature methods. NMR spectra were run on Varian EM-390 (^1H) (90 MHz), Varian FT-80 (^{31}P and ^{13}C at 32.384 and 20.0 MHz, respectively), Bruker WH-90 (^{31}P at −80 °C), and Nicolet FT-200 (^{31}P) instruments. IR spectra were run on a Perkin-Elmer 1330. Simulation of the $^{31}P\{^1H\}$ spectrum was done on a Nicolet NIC-80 using the Nicolet NMRCAL program.

$[Rh(\mu\text{-}t\text{-}Bu_2P)CO]_3$. A solution of t-Bu_2PLi in THF (0.97 g, 6.4 mmol, in 7.0 mL) was slowly added to a solution of $[Rh(CO)_2Cl]_2$ (1.24 g, 3.20 mmol) in THF (40 mL) at −78 °C. The solution was allowed to warm slowly to −50 °C over a 1-h period. Volatile materials were then removed under vacuum at −50 °C. The residue was extracted into hexane (30 mL) at room temperature, and the resulting deep red solution was filtered. The solution was evaporated to 15 mL under vacuum and then transferred to a short column (3 × 10 cm) of 80–325 mesh chromatographic grade alumina. The column was eluted with hexane. Two dark red bands developed. The first contained the dinuclear complex $[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$[4] and the second $[Rh(\mu\text{-}t\text{-}Bu_2P)CO]_3$. The fractions were collected, and that which contained the trimer was evaporated to ca. 15 mL and cooled at −40 °C for 12 h. The dark red-brown crystals were collected and dried under vacuum: yield 0.53 g, 30% based on $[Rh(CO)_2Cl]_2$; mp 223–225 °C dec; IR (Nujol mull, KBr plates) 1951 s, 1297 m, 1166 m, 1015 w, 801 w cm^{-1}; IR (hexane solution) (matched KBr cells) 1957 s, br, cm^{-1}; NMR ^1H δ 1.6 m (t-Bu) in C_6D_6 at ambient temperature referenced to external Me_4Si (δ 0.0), $^{31}P\{^1H\}$ δ 369.0 in C_6D_6 at ambient temperature referenced to external 85% H_3PO_4 (δ 0.0) (positive is downfield), $^{13}C\{^1H\}$ δ 47.11 s (CMe_3), 32.41 s ($C\mathit{Me}_3$) in C_6D_6 relative to Me_4Si. CO NMR resonances were not observed even with added $Cr(acac)_3$ and extended acquisition times.

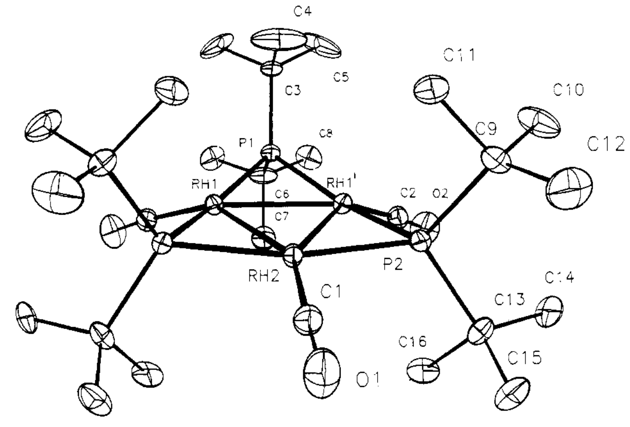

Figure 1. Molecular structure of $[Rh(\mu\text{-}t\text{-}Bu_2P)CO]_3$.

Table I. Bond Distances (Å) and Bond Angles (deg) in $[Rh(\mu\text{-}t\text{-}Bu_2P)CO]_3$

Distances			
Rh(1)–Rh(1)	2.638 (2)	Rh(1)–Rh(2)	2.659 (2)
Rh(1)–P(1)	2.273 (5)	Rh(1)–P(2)	2.295 (4)
Rh(1)–C(2)	1.85 (2)	Rh(2)–P(2)	2.273 (3)
Rh(2)–C(1)	1.82 (2)		

Angles			
Rh(1)–Rh(1)–Rh(2)	60.26 (3)	Rh(1)–P(1)–Rh(1)	70.9 (2)
Rh(2)–Rh(1)–P(2)	54.02 (8)	Rh(2)–Rh(1)–P(1)	112.98 (9)
Rh(2)–Rh(1)–C(2)	143.9 (5)	P(1)–Rh(1)–P(2)	158.8 (2)
P(2)–Rh(1)–C(2)	98.4 (5)	P(1)–Rh(1)–C(2)	99.7 (5)
Rh(1)–Rh(2)–Rh(1)	59.48 (6)	Rh(1)–Rh(2)–P(2)	54.78 (9)
Rh(1)–Rh(2)–C(1)	149.8 (1)	P(2)–Rh(2)–C(1)	95.9 (1)

X-ray Crystallography. The data crystal was sealed under nitrogen in a 0.5-mm o.d. Lindemann glass capillary. Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation. The diffracted intensities were collected by the ω–2θ scan technique in a manner similar to that previously described.[7] Crystal data: space group orthorhombic $Cmc2_1$ with $a = 19.563$ (8), $b = 15.633$ (7), and $c = 11.684$ (6) Å, mol wt 828.45, cell volume 3495.1 Å^3, $Z = 4$, calculated density 1.57 g cm^{-3}, crystal dimensions 0.20 × 0.30 × 0.35 mm. Calculated $\mu = 15.2$ cm^{-1}; least-squares refinement based on 998 observed reflections (1276 measured) ($2\theta \leq 44°$; $I \geq 3\sigma(I)$) gave $R = 0.036$ and $R_w = 0.043$. Hydrogen atoms were not located, and the non-hydrogen atoms were refined with anisotropic thermal parameters. The number of parameters varied was 172. Although the data to parameter ratio is low (5.8), the crystal scattered poorly at high angles. Further data are therefore unlikely to affect the key metal–metal, metal–phosphorus, or metal–carbonyl distances or angles. No absorption correction was applied since a χ-scan study revealed no problem. Systematic absences allowed the space group to be either $Cmcm$ or $Cmc2_1$. However, with four molecules per unit cell, additional crystallographic considerations had to be taken into account. The point symmetry in $Cmcm$ must be mm, while only a single mirror plane is required in $Cmc2_1$. The latter seemed more likely, and the correctness of the choice was borne out by the refinement. (In Figure 1, it can clearly be seen that the

---

(1) University of Alabama.

(2) The University of Texas.

(3) Jones, R. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E.; Rogers, R. D. *Organometallics* **1982**, *1*, 1721.

(4) Jones, R. A.; Wright, T. C.; Atwood, J. L.; Hunter, W. E. *Organometallics*, in press.

(5) Issleib, K.; Krech, F. *J. Organomet. Chem.* **1968**, *13*, 283.

(6) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 211.

(7) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45.

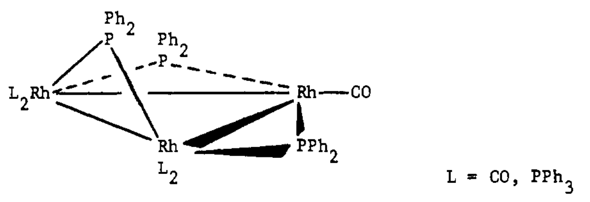

Figure 2. Overall structures of $Rh_3(\mu\text{-}Ph_2P)_3(CO)_5$ and $Rh_3(\mu\text{-}Ph_2P)_3(CO)_3(PPh_3)_2$ (from ref 12 and 13).

carbonyl group, C(2)–O(2), is well below the plane of the three Rh atoms; coplanarity would be required in *Cmcm*.) The inverse configuration was found to produce a slightly lower *R* value, and those coordinates are the basis for the values in Table I.

Results and Discussion

The interaction of $[Rh(CO)_2Cl]_2$ with 1 equiv of $t\text{-}Bu_2PLi$ in tetrahydrofuran at −78 °C yields a deep red homogeneous solution containing a mixture of compounds. Deep red-brown crystals of $[Rh(\mu\text{-}t\text{-}Bu_2P)CO]_3$ may be isolated on cooling (−20 °C) the hexane solution following chromatography (see Experimental Section). The compound is quite air sensitive in solution although air stable for short periods in the solid state. The molecular structure and labeling scheme are shown in Figure 1. Bond distances and angles are presented in Table I. The atomic positional parameters thermal parameters, and observed and calculated structure factors are available as supplementary material. Until recently few triangular Rh_3 clusters were known. Well-characterized Rh_3 clusters having $C_5H_5^-$, CO, or $P(OR)_3$ and H such as $[CpRh(CO)]_3$,[8] $Rh_3(CO)_{10}^-$,[9] $Cp_2Rh_3(CO)_4^-$,[10] and $[HRh(P(OMe)_3)_2]_3$[11] have been described. In addition, pyrolysis of $RhH(CO)PPh_3)_3$ in nonane at 120 °C yielded $Rh_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_3)_2$[12] and the interaction of $[Rh(CO)_2Cl]_2$ with PPh_2H in benzene in the presence of Et_2NH gave $Rh_3(\mu\text{-}PPh_2)_3(CO)_5$.[13]

The structure of $[Rh(\mu\text{-}t\text{-}Bu_2P)CO]_3$ as revealed by X-ray crystallography has two features that make it notably different from the other Ph_2P-bridged rhodium trimers. The central Rh_3P_3 core is virtually planar, and the rhodium atoms are *all* coordinatively unsaturated since each has only one terminal CO bonded to it. The molecule has a mirror plane that lies perpendicular to the Rh_3 plane, passes through a unique rhodium atom (Rh(2)), bisects the bond between the other two rhodium atoms (Rh(1) and Rh(1)′) and passes through the phosphorus atom (P(1)) of the $t\text{-}Bu_2P$ unit, which bridges Rh(1) and Rh(1)′. Although the $Rh_3P_3(CO)_3$ core is virturally planar, the three phosphorus nuclei all lie slightly out of the Rh_3 plane while the three carbonyl units are all slightly bent to the other side of this plane[13] (as viewed in Figure 1). The Rh–Rh distances (2.638 (2) and 2.659 (2) Å) are in the range expected for single rhodium–rhodium bonds.

In contrast, for the Ph_2P^- complexes, a unique Ph_2P^- bridge lies almost orthogonal to the remaining Rh_3P_2 unit (virtually coplanar). The rhodium atom that is not bridged by the unique Ph_2P bridge has one CO ligand and is coordinatively unsaturated. The remaining rhodium atoms each carry two two-electron donor ligands (CO or PPh_3) and are thus formally coordinatively saturated 18-electron atoms. The reason for the structural features in these Ph_2P^- systems are not yet clear[11,12] (see Figure 2).

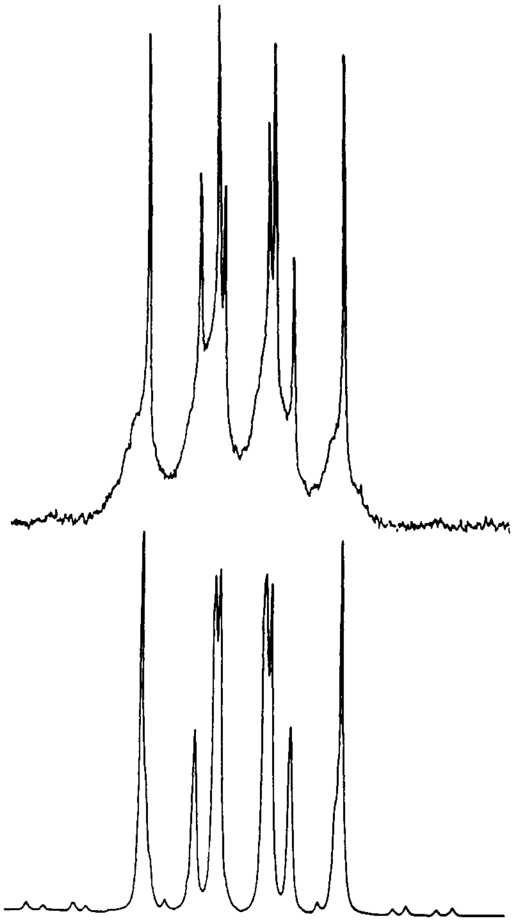

Figure 3. Simulated (bottom) and observed (top) $^{31}P\{^1H\}$ NMR spectra of $[Rh(\mu\text{-}t\text{-}Bu_2P)CO]_3$ at 80.962 MHz and ambient temperature.

In the case of $[Rh(\mu\text{-}t\text{-}Bu_2P)CO]_3$ however it appears that steric factors largely determine the observed structure. Study of model compounds shows that the bulky *tert*-butyl groups attached to phosphorus allow sufficient room on each rhodium atom for the coordination of only one CO and also prevent major distortions of the Rh_3P_3 framework from planarity. We have also synthesized dinuclear complexes of $t\text{-}Bu_2P$ in which the central $M(\mu\text{-}t\text{-}Bu_2P)_2M$ unit is accurately planar[3,4] unlike other Ph_2P-bridged complexes in wich a butterfly arrangement of the M_2P_2 core is often encountered.[14] It is interesting to note that the geometry adopted by the Rh_3P_3 core in $[Rh(\mu\text{-}t\text{-}Bu_2P)CO]_3$ does bear a slight similarity to those of $Rh_3(\mu\text{-}Ph_2P)_3(CO)_3(PPh_3)_2$ and $Rh(\mu\text{-}Ph_2P)_3(CO)_5$ in that one $t\text{-}Bu_2P$ bridge is noticeably more distorted from the Rh_3 plane than the other two (16.56° vs. 5.11°). Since the slight distortions from planarity are so small, they may be due to packing forces in the crystal structure.

In solution infrared and NMR data show only one type of $\mu\text{-}t\text{-}Bu_2P$ and CO unit. Two situations could account for these observations: (i) the molecule could have all Rh, P, and CO atoms accurately planar in solution, or (ii) the molecule could be rapidly fluxional via facile bending motion of the $t\text{-}Bu_2P$ and CO groups. Unfortunately the NMR spectra are unchanged to −90 °C and the IR spectrum shows a rather broad single absorption which, however, may be due to several almost

---

(8) Paulus, E. F.; Fischer, E. O.; Fritz, H. P.; Schuster-Woldan, H. *J. Organomet. Chem.* **1967**, *10*, P3. Mills, O. S.; Paulus, E. F. *Ibid.* **1967**, *10*, 331. Mills, O. S.; Paulus, E. F. *Chem. Commun.* **1966**, 815.

(9) Chini, P.; Martinengo, S. *J. Chem. Soc. D.* **1969**, 1092.

(10) Jones, W. D.; White, M. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 6772.

(11) Brown, R. K.; Williams, J. M.; Sivak, A. J.; Muetterties, E. L. *Inorg. Chem.* **1980**, *19*, 370.

(12) Billig, E.; Jamerson, J. D.; Pruett, R. L. *J. Organomet. Chem.* **1980**, *192*, C49.

(13) Haines, R. J.; Steen, N. D. C. T.; English, R. B. *J. Organomet. Chem.* **1981**, *209*, C34.

(14) The dihedral angles formed by each set of RhRhP planes with the Rh_3 plane are as follows: Rh(1)–Rh(1)–P(1), 16.56°; Rh(1)–Rh(2)–P(1), 5.11°. Angles between the CO units and the Rh_3 plane: C(2), 157°; C(1), 175°.

coincident bands. The data, therefore, do not allow us to differentiate between (i) and (ii). The $^{31}P\{^1H\}$ NMR at room temperature (benzene-d_6 solution) and at −80 °C (toluene-d_8) shows a multiplet shifted well downfield (δ369.0 relative to 85% H_3PO_4). Similar large downfield shifts have been noted for other phosphides which bridge metal-metal bonds.[15]

Computer simulation of the spectrum (Figure 3) gives the following values of the magnitudes of the coupling constants for this A, A′, A″, X, X′, X″ spin system: $^1J_{\text{Rh-P}} = 130$ Hz, $^2J_{\text{Rh-P}} = 8$ Hz, and $^2J_{\text{P-P}} = 120$ Hz.

Both large (ca. 150 Hz) and small (ca. 5 Hz) values of $^1J_{\text{Rh-Rh}}$ have been estimated from ^{31}P NMR data.[16] However, we were unable to identify any faint "wing tips" in the observed spectrum, which would have enabled an accurate value of $^1J_{\text{Rh-Rh}}$ to have been determined, the actual value of which could be negative, zero, or positive. The appearance of the simulated spectrum did not change considerably when $^1J_{\text{Rh-Rh}}$ was varied from −10 to +100 Hz. Figure 3 shows the simulated spectrum with $^1J_{\text{Rh-Rh}} = -10$ Hz.

Further studies into the reaction chemistry of $[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)]_3$ and related complexes are in progress.

Acknowledgment. We thank the Dow Chemical Co., Midland, MI (R.A.J.), the Robert A. Welch Foundation (R.A.J.), and the National Science Foundation (J.L.A.) for financial support. We also thank Johnson-Matthey Ltd. for a loan of rhodium trichloride and one reviewer for helpful comments on NMR.

Registry No. $[Rh(\mu\text{-}(t\text{-}Bu)_2P)CO]_3$, 84433-32-9; $[Rh(CO)_2Cl]_2$, 14523-22-9; $[Rh(\mu\text{-}(t\text{-}Bu)_2P)(CO)_2]_2$, 84454-21-7; Rh, 7440-16-6.

Supplementary Material Available: Tables of all bond distances and angles, thermal parameters, atomic positions in fractional coordinates, and observed and calculated structure factors for $[Rh(\mu\text{-}t\text{-}Bu_2P)CO]_3$ (9 pages). Ordering information is given on any current masthead page.

---

(15) See for example: Ginsburg, R. E.; Rothrock, R. K.; Finke, R. G.; Collman, J. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1979**, *101*, 6550 and references therein.

(16) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229 and references therein.

(17) Mague, J. T.; Sanger, A. R. *Inorg. Chem.* **1979**, *18*, 2060. Cowie, M.; Mague, J. T.; Sanger, A. R. *J. Am. Chem. Soc.* **1978**, *100*, 3628. Lawson, R. J.; Shapley, J. R. *Inorg. Chem.* **1978**, *17*, 2963.

Contribution from the Institute of Chemistry,
Academy of Sciences of Moldavian SSR,
277028 Kishinev, USSR

Critical Comments on the Papers "Reanalysis of the Thermal, Magnetic, and Spectral Properties of $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl\cdot 6H_2O$ on the Basis of an Intercluster Spin-Exchange Model"[1] and "Magnetic Properties and Mössbauer Spectra of Several Iron(III)–Dicarboxylic Acid Complexes"[2]

B. S. Tsukerblat,* M. I. Belinskii, and B. Ya. Kuyavskaya

Received December 15, 1981

The physical properties of trinuclear transition-metal carboxylates of the $[M_3O(RCOO)_6(H_2O)_3]X$ type (M = Cr(III), Fe(III); RCOO = carboxylate ion; X = Cl, ClO_4, NO_3, RCOO) have attracted the attention of investigators for more than 20 years. Numerous magnetic, heat capacity, optical, radiospectroscopic, and Mössbauer data (see ref 3 and 4 and references therein) have been accounted for by the Heisenberg model, which also includes relatively small terms of non-Heisenberg interactions (antisymmetric and biquadratic exchange interactions). Nevertheless, in spite of the fact that the theory, including all actual physical interactions, has achieved certain success, the problem of adequate interpretation of all experimental data is far from being settled. We should mention, in particular, the absence of simultaneous interpretation of the data on magnetic susceptibility,[5,6] spin heat capacity,[7,8] and ESR spectra[9,10] of the most investigated trimeric chromium carboxylates. The properties of these compounds were discussed on the basis of the Heisenberg–Dirac–Van Vleck Hamiltonian

$$\mathcal{H} = -2J_0(s_1s_2 + s_2s_3 + s_3s_1) - 2J_1s_1s_2 \qquad (1)$$

where J_0 and J_1 are the isotropic exchange interaction parameters. The weak deviation from the trigonal cluster's symmetry described by parameter J_1 plays an essential role in the temperature dependence of the thermodynamic values and ESR spectra. The magnetic susceptibility data on $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl\cdot 6H_2O$ crystals[5] led to the values $J_0 = 10.5$ cm^{-1} and $J_1 = 2.5$ cm^{-1}. The agreement of the spin capacity temperature dependence was achieved on the assumption of the presence of two types of clusters with the parameters $J_0 = 10.5$, $J_1 = 1.57$ cm^{-1} and $J_0 = 10.5$, $J_1 = -0.36$ cm^{-1},[8] and the ESR spectra interpretation was carried out in ref 10 on the assumption that the ground-state splitting is less than 0.31 cm^{-1}. Experimental data referring to every class of physical phenomena have found their explanations in the framework of the intercluster interaction model. To describe these data quantitatively, one has to accept several different sets of exchange parameters.

The main aim of the papers under discussion[1,2] is to reanalyze the magnetic, thermal, and spectral properties of trimeric chromium(III) and iron(III) clusters. The authors have introduced a model that includes the exchange interaction between two trinuclear units in addition to intramolecular exchange terms.

Let us discuss the need to complicate the theory of magnetic properties by taking into account the intercluster interactions. A set of experimental data indicates the absence of an appreciable contribution of the interactions mentioned above. One should specifically refer to the paper of Schriempf and Friedberg,[6] in which it has been shown that to $T = 0.38$ K the temperature dependence of the magnetic susceptibility of the basic chromium acetate $[Cr_3O(CH_3COO)_3(H_2O)_3]Cl\cdot 5H_2O$ follows the Curie–Weiss law. The obtained value of the Weiss constant $\Theta = -0.13$ K determines the upper limit of the intercluster interaction energy. The analogous conclusion ($\Theta = -0.12$ K) concerning the trimetric iron carboxylate had been obtained by Takano.[11] Therefore, it follows that the analysis of available experimental data is not likely

---

(1) Wrobleski, J. T.; Dziobkowski, C. T.; Brown, D. B. *Inorg. Chem.* **1981**, *20*, 684.

(2) Dziobkowski, C. T.; Wrobleski, J. T.; Brown, D. B. *Inorg. Chem.* **1981**, *20*, 671.

(3) Hatfield, W. E. In "Theory and Application of Molecular Paramagnetism"; Wiley: New York, 1976; Chapter 7, p 349.

(4) Catterick, J.; Thornton, P. *Adv. Inorg. Chem. Radiochem.* **1977**, *20*, 291.

(5) Wucher, J.; Cijsman, H. M. *Physica (Amsterdam)* **1954**, *20*, 361.

(6) Schriempf, J. T.; Friedberg, S. A. *J. Chem. Phys.* **1964**, *40*, 296.

(7) Wucher, J.; Wasscher, J. D. *Physica (Amsterdam)* **1954**, *20*, 721.

(8) Sorai, M.; Tachiki, M.; Suga, H.; Seki, S. *J. Phys. Soc. Jpn.* **1971**, *30*, 750.

(9) Clad, R.; Wucher, J. *C.R. Hebd. Seances Acad. Sci.* **1965**, *260*, 4318.

(10) Yablokov, Yu. V.; Gaponenko, V. A.; Zelentsov, V. V. *Sov. Phys.–Solid State (Engl. Transl.)* **1971**, *13*, 1293. Yablokov, Yu. V.; Gaponenko, V. A.; Ablov, A. V.; Zhikhareva, T. N. *Fiz. Tverd. Tela (Leningrad)* **1973**, *15*, 337. Yablokov, Yu. V.; Gaponenko, V. A.; Zelentsov, V. V.; Suvorova, K. M. *Solid State Commun.* **1974**, *14*, 131.

(11) Takano, M. *J. Phys. Soc. Jpn.* **1972**, *33*, 1312.

0020-1669/83/1322-0995$01.50/0