ing region. Four bands were observed, one of which is very weak. For the $Ru_2(CO)_4$ group found, with C_2 symmetry, four infrared-active CO stretching modes would be expected. One of these would likely be essentially the antisymmetrically coupled stretching of the two CO groups (1A and 2A) which are approximately perpendicular to the plane of the Ru_3 triangle. This mode would have only a slight dipolar transition moment, thus accounting for the one extremely weak band.

Lastly, it may be noted that the $(C_8H_8)_2Ru_3(CO)_4$ molecule is dissymmetric in its idealized C_2 symmetry. Since it crystallizes in enantiomeric crystals, it would perhaps be feasible to study the rate of racemization, or at least to set a lower limit on it, by preparing solutions from individual single crystals. Racemization may well be a very rapid process, since it could readily be accomplished in the following way. The CO(1A) and CO(2A) groups could swing toward the center of the Ru(1)–Ru(2) bond and become bridging CO groups. This sort of interconversion of terminal with bridging systems is well known, for example, in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$,[21] $[(\pi\text{-}C_5H_5)Ru(CO)_2]_2$,[21] and $Co_2(CO)_8$.[22] If, at the same time as the bridges form, the C_8H_8 rings move slightly so that the plane of the Ru_3 triangle becomes a bisector of the mean plane of each ring, an intermediate without chirality will be formed, which may then return to either enantiomer of the chiral structure with equal probability, thereby accomplishing racemization. Thus, a study of the rate of racemization of the $(C_8H_8)_2Ru_3(CO)_4$ molecule would be equivalent to a study of the rate of interconversion of the bridged and nonbridged $Ru_2(CO)_4$ systems, and would therefore be of fundamental interest.

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[21] F. A. Cotton and G. Yagupsky, *Inorg. Chem.*, **6**, 15 (1967).

[22] K. Noack, *Spectrochim. Acta*, **19**, 1925 (1963).

Transition Metal Carbonyl Anions. I. The Course of the Reduction of Chromium Hexacarbonyl[1]

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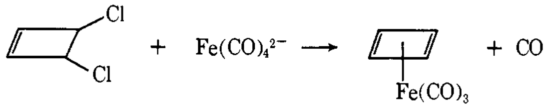
Contribution from the Department of Chemistry, University of California, Santa Barbara, California 93106. *Received May 23, 1968*

Abstract: In order to reveal the chemical and physical properties of group VI transition metal carbonyl anions, a study of the chromium hexacarbonyl reduction has been undertaken. Chromium hexacarbonyl was reduced in tetrahydrofuran and hexamethylphosphoramide with sodium, potassium, and cesium amalgam, phenanthrene-sodium, and trimesitylboron sodium. An extensive comparison of infrared spectra suggests the formation of $[Cr_2(CO)_{10}]^{2-}$, $[Cr(CO)_5]^{2-}$, $[Cr(CO)_5HMPT]^{2-}$, and $[Cr_2(CO)_9]^{4-}$ ions. The conditions for isolation and purification of the ions are discussed.

The carbonylmetallate ions of group VI[2] transition metal elements and their organometallic derivatives are potentially useful in the synthesis of metal–metal and metal–metalloid bonds.[3] With a combination of suitable ligands these materials are intriguing starting points toward the synthesis of catenated transition metal compounds, or "synthetic metals" as they might be called. These, in turn, offer the possibility of studying solid-state physical and chemical properties such as magnetic behavior and heterogeneous catalysis.

In other instances, the carbonylmetallate ions may be valuable in the preparation of organometallic compounds. Such a case in particular has been the eminently successful role of these ions in the synthesis of cyclobutadiene–metal carbonyl complexes.[4]



From another aspect the anions are of interest because they are isoelectronic with known metal carbonyls. For example, $[Cr_2(CO)_{10}]^{2-}$ [5] is isoelectronic with $Mn_2(CO)_{10}$; $[Cr(CO)_5]^{2-}$ is related to the unstable species $Mn(CO)_5$ and to the known $Fe(CO)_5$ molecule. Other ions such as $[Cr_2(CO)_9]^{2-}$ and $[Re_2(CO)_9]^{-}$ [6,7] are related and $[Cr_2(CO)_9]^{4-}$ is isoelectronic with $Fe_2(CO)_9$.

Behrens and his coworkers[8–11] have reported no less than five different carbonylmetallate ions of group VI from various synthetic routes. Some of these ions are $[Cr(CO)_5]^{2-}$, $[Cr_2(CO)_{10}]^{2-}$, $[Mo_2(CO)_9]^{4-}$, $[Cr_3(CO)_{14}]^{2-}$, and $[Cr_2H(CO)_{10}]^{-}$.

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[1] Presented in part at the Third International Organometallic Symposium at Munich, Germany, Aug 29–Sept 1, 1967.

[2] (a) R. B. King, *Advan. Organometal. Chem.*, **2**, 157 (1964); (b) F. Calderazzo, R. Ercoli, and G. Natta, "Organic Synthesis Via Metal Carbonyls," Vol. 1, I. Wender and P. Pino, Ed., John Wiley and Sons, Inc., New York, N. Y., 1968, p 150.

[3] (a) R. E. Dessy, and P. M. Weissman, *J. Am. Chem. Soc.*, **88**, 5124 (1966); (b) U. Anders and W. A. G. Graham, *ibid.*, **89**, 539 (1967); (c) J. K. Ruff, *Inorg. Chem.*, **6**, 2080 (1967).

[4] R. G. Amiet, P. C. Reeves, and R. Pettit, *Chem. Commun.*, 1208 (1967).

[5] R. G. Hayter, *J. Am. Chem. Soc.*, **88**, 4376 (1966).

[6] G. W. Parshall, *ibid.*, **86**, 361 (1964).

[7] R. W. Harrill and H. D. Kaesz, *Inorg. Nucl. Chem. Letters*, **2**, 69 (1966).

[8] H. Behrens and R. Weber, *Z. Anorg. Allgem. Chem.*, **291**, 123 (1957).

[9] H. Behrens and J. Vogl, *Chem. Ber.*, **96**, 2220 (1963).

[10] H. Behrens and W. Haag, *ibid.*, **94**, 312 (1961).

[11] H. Behrens and W. Haag, *ibid.*, **94**, 320 (1961).

While not all are easily synthesized, Hayter[5] has recently reported on the preparation and chemical properties of $[Cr_2(CO)_{10}]^{2-}$ and $[Cr_2H(CO)_{10}]^{-}$. In general the preparation of the carbonylmetallate ions utilizes a reducing agent such as alkali metal amalgam or alkali metal in liquid ammonia. However, such reagents often promote the formation of undesirable by-products. Lewis acid–base adducts may form in liquid ammonia, and mercury can influence the course of the reaction.[12] It is the course of the reduction, with a special emphasis on the isolation of stable products, that forms the basis of this paper. Thus we hope to effectively exploit the synthetic utility of these ions by delineating the methods by which they can be made in good yield.

Results and Discussion

The $[Cr_2(CO)_{10}]^{2-}$ Ion. The reaction of group VI metal hexacarbonyls with sodium in tris(dimethylamino)phosphine oxide (hexamethylphosphoramide, HMPT)[13] gives deep red solutions. When chromium hexacarbonyl in HMPT was reduced with sodium metal, a bright yellow, crystalline, air-sensitive solid was isolated from the red reaction mixture. Conversion of this sodium salt to the tetraethylammonium salt produced a yellow compound which was identical in all respects with $[(C_2H_5)_4N]_2[Cr_2(CO)_{10}]$ reported by Hayter.[5] Figure 1 illustrates the infrared spectra of the ion in the carbonyl stretching region, and Table I lists the corrected infrared frequencies observed.

Table I. Infrared Carbonyl Stretching Frequencies (cm^{-1}) for $Cr_2(CO)_{10}{}^{2-}$ with Various Cations and Solvents

$[Na]_2[Cr_2(CO)_{10}]$ in THF		$[Na]_2[Cr_2(CO)_{10}]$ in CH_3CN or HMPT		$[(C_2H_5)_4N]_2$-$[Cr_2(CO)_{10}]$ in THF	
1903	A	1897	A′	1903	A″
1880	B	1869	B′	1880	B″
1851	F	1776	C′	1776	C″
1801	E			1721	D′
1776	C				
1756	D				

In order to verify the synthesis in HMPT the $[Cr_2(CO)_{10}]^{2-}$ (I) ion was also prepared according to the reactions

$$[(C_2H_5)_4N][Cr(CO)_5Br] + Na(Hg) \xrightarrow{THF} [(C_2H_5)_4N][Na][Cr_2(CO)_{10}]$$

$$[(C_2H_5)_4N][Cr(CO)_5H] + KO\text{-}t\text{-}Bu \xrightarrow{THF} [(C_2H_5)_4N][K][Cr_2(CO)_{10}]$$

$$[(C_2H_5)_4N][Cr(CO)_5H] + NaBH_4\ (excess) \xrightarrow{THF} [(C_2H_5)_4N][Na][Cr_2(CO)_{10}$$

In each case the infrared spectrum of the major product isolated was identical with that of the product obtained by reduction of chromium hexacarbonyl in HMPT.

The tetraethylammonium or sodium salt of I readily dissolves in HMPT or CH_3CN to give spectrum b shown in Figure 1. A three-band infrared pattern strongly suggests a D_{4d} or D_{4h} symmetry for I. Moreover, the X-ray structure of I definitely supports chromium–chromium[14] bond formation in the solid state with

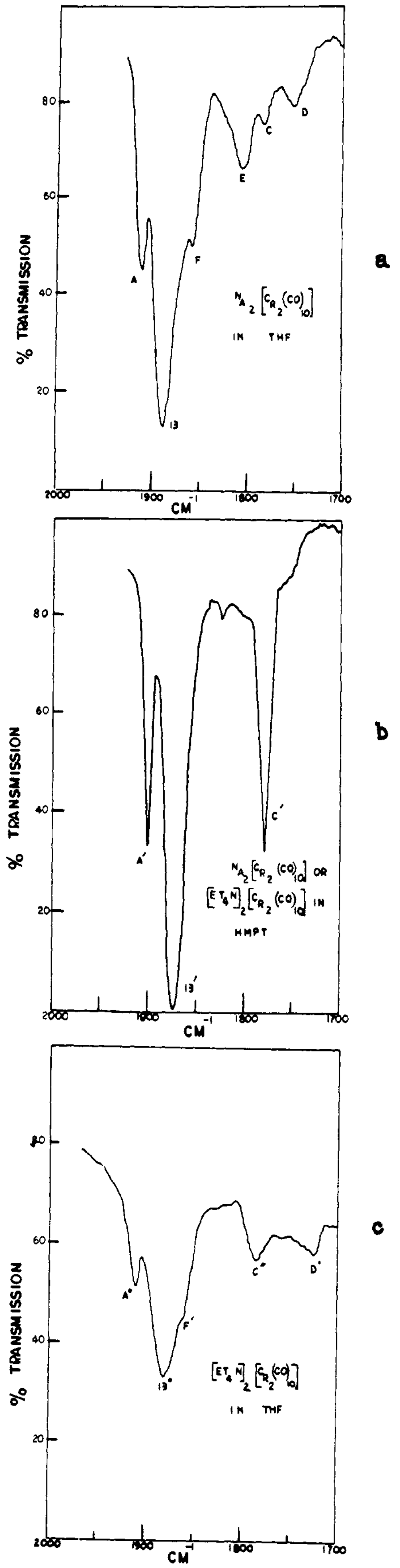

Figure 1. Infrared spectra in the carbonyl stretching region for $[Cr_2(CO)_{10}]^{2-}$.

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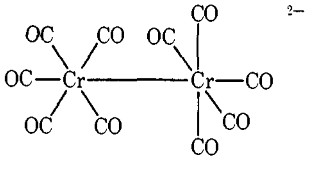
(12) T. A. Manuel, *Advan. Organometal. Chem.*, 3, 181 (1965).

(13) H. Normant, *Angew. Chem.*, 79, 1029 (1967); *Angew. Chem. Intern. Ed. Engl.*, 6, 1046 (1967).

(14) L. F. Dahl, private communication, 1968. We are grateful to Professor Dahl for informing us of this result prior to publication.

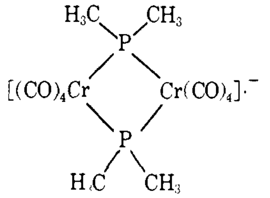


I, D_{4d}

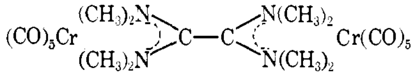
staggering of the pentacarbonyl moieties. When the tetraethylammonium salt of I was dissolved in tetrahydrofuran (THF), spectrum c was obtained. The same spectrum, c, may be obtained when HMPT or CH_3CN is removed from I by precipitating the ion with hexane and redissolving it in THF. Thus these solvents do not permanently alter the structure of I at room temperature. However, spectra a, b, and c illustrate that various solvents and cations play an important role in the appearance of the infrared spectrum of I. The slow disappearance of band, D′ and F′ in spectrum c was observed when the infrared spectrum of I was recorded in CH_3CN–THF (70–30% by weight). Furthermore spectrum a, which is the sodium salt of I in THF, gradually became like spectrum b as the concentration of HMPT was increased. Thus bands D, E, and F disappeared while band C grew in intensity to C′. A weak but persistent band at 1820 cm^{-1} may be provisionally assigned to a ^{13}C mode of the major peak at 1869 cm^{-1}. This is consistent with the Teller–Redlich rule and the natural abundance of isotopes.

In other carbonylmetallate ions, especially the $[Co(CO)_4]^-$ anion, Edgell and coworkers[15] have shown that the presence of ion pairs can alter the shape and shift the frequency of the carbonyl stretching bands. Thus the anion and cation are important in determining the character of the carbonyl stretching region in carbonylmetallate ions. Furthermore, solvent factors alone can influence the carbonyl stretching region.[16] It is interesting to note that the most polar solvents studied give the most narrow half-band width and also the correct number of bands predicted by symmetry for the ion. We interpret this to mean that the ions[5] are virtually completely dissociated in HMPT, and the electrostatic interaction between solvated cation and anion is greatly diminished. Then the cation does not distort the anion sufficiently from its idealized symmetry so that additional carbonyl stretching bands are observed. A similar behavior of anions and radical anions in HMPT has been reported by Szwarc and coworkers.[17]

Although band C′ in spectrum b and especially D′ in spectrum c lie in what has been commonly called the bridging region,[5,16b] this does not unequivocally prove the existence of bridge CO groups. Other carbonyl ions such as $[C_5H_5V(CO)_3]^{2-}$ [2b] and $[Fe(CO)_4]^{2-}$ [2b] have low infrared stretching frequencies, 1748, 1645, and 1730 cm^{-1}, respectively, and CO bridge groups are presumably not involved. An equally satisfying rationale for the low carbonyl stretching frequency in these ions is that the low formal oxidation state supports a high metal–carbon bond order and a low carbon–oxygen bond order. This means that the carbon–oxygen bond will be weaker; hence, the vibrational frequency will be lower than in the neutral compounds. This has been nicely illustrated by the following bridged complex,[18] which is related to I, except that two CO groups have been removed. The carbonyl stretching frequencies have moved to longer wavelengths by ~100 cm^{-1} compared to the neutral compound (ν_{CO}(neutral) 2015, 1950 cm^{-1}, ν_{CO}(radical anion) 1900, 1870 cm^{-1}).



Further evidence that certain cations distort anion I even to the point of metal–metal cleavage comes from the observation that the reaction of H_3O^+ and I gives $[(CO)_5Cr\text{-}H\text{-}Cr(CO)_5]^-$ (ν_{CO} 2020, 1930, 1875 cm^{-1}). When *anhydrous* LiCl or LiBr was stirred with the tetraethylammonium salt of I in cold THF or HMPT, bands at 2020, 1930, and 1875 cm^{-1} slowly appeared in the infrared spectrum, although the peaks characteristic of I never completely disappeared. The exact nature of the species responsible for the bands in HMPT is not clear, although most $[Cr(CO)_5L]$ derivatives give an infrared band pattern like $[Cr_2H(CO)_{10}]^-$.[19] Although cations such as Hg^{2+} and $[Ni(phen)_3]^{2+}$ may behave as oxidizing agents[5] to I, other cations such as octamethylamidinium bromide (TDME, Br_2)[20] distort I enough to promote a reaction. When the sodium salt of I in *cold, dry* ethanol was mixed with (TDME, Br_2), a bright red solid (contaminated with NaBr) was isolated. The solid decomposed in air and became yellow in water.[21] The infrared spectrum in THF gave a band pattern similar to other $[Cr(CO)_5L]$ derivatives.[22] However, other products such as $Cr(CO)_5TDME$ are present, since uv irradiation of TDME with $Cr(CO)_6$ in THF gave a compound whose infrared spectrum presented some of the bands seen in the spectrum of the product from the metathesis reaction. It is known that TDME does not reduce $Cr(CO)_6$. We provisionally propose that the following species is formed.



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(15) W. F. Edgell, M. T. Yang, and N. Koizumi, *J. Am. Chem. Soc.*, **87**, 2563 (1965); W. F. Edgell, A. T. Watts, J. Lyford, IV, and W. M. Risen, Jr., *ibid.*, **88**, 1815 (1966).

(16) (a) F. A. Cotton and G. Yagupsky, *Inorg. Chem.*, **6**, 15 (1967); (b) D. M. Adams, "Metal-Ligands and Related Vibrations," St. Martins Press, New York, N. Y., 1968, p 110.

(17) A. Cserhegyi, J. Chaudhuri, E. Franta, J. Jagur-Grodzinski, and M. Szwarc, *J. Am. Chem. Soc.*, **89**, 7129 (1967).

(18) R. E. Dessy, R. Kornmann, C. Smith, and R. Hayter, *ibid.*, **90**, 2001 (1968).

(19) It is conceivable that $[Cr_2H(CO)_{10}]^-$ could be formed from the decomposition of THF in the presence of compound I and LiBr, although we could find no evidence in the nmr for $[Cr_2H(CO)_{10}]^-$. The reaction of $Cr(CO)_6$ with Na(Hg) (*cf.* H. E. Podall, H. B. Prestridge, and H. Shapiro, *ibid.*, **83**, 2056 (1961)) in boiling THF gave solutions whose infrared spectra showed the presence of bands similar to those reported for $[Cr_2H(CO)_{10}]^-$. Even during conversion of the sodium salt to the tetraethylammonium salt in CH_3CN, a THF-soluble portion was isolated whose infrared spectrum showed peaks similar to $[Cr_2H(CO)_{10}]^-$. However, if THF was completely eliminated from the synthesis of I, the bands characteristic of $[Cr_2H(CO)_{10}]^-$ did not appear until lithium halide was added to the HMPT or THF solution of I. It is now known that lithium halide salts will effectively cleave organic epoxides in the presence of HMPT; *cf.* B. Rickborn and R. Gerkin, *ibid.*, 90, 4193 (1968).

(20) R. B. King, *Inorg. Chem.*, 4, 1518 (1965).

(21) The ethanol must be cold and dry or else $[Cr_2H(CO)_{10}]^-$ is formed. When the red solid is warmed in ethanol or allowed to stand for any length of time in ethanol, the major product is $[Cr_2H(CO)_{10}]^-$.

(22) C. R. Dobson, I. W. Stolz, and R. K. Sheline, *Advan. Inorg. Chem. Radiochem.*, **8**, 1 (1966).

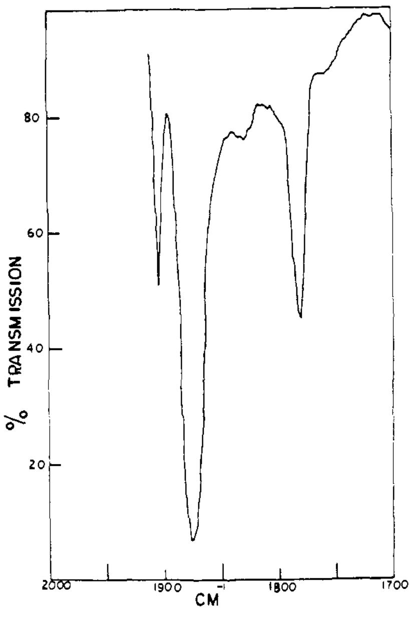


Figure 2. Infrared spectrum of I in the carbonyl stretching region in HMPT after reaction with sodium.

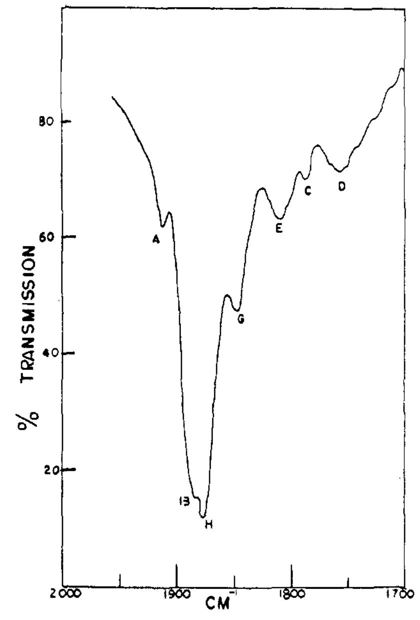
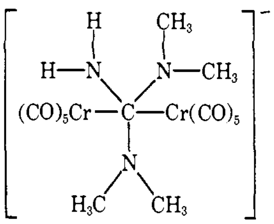


Figure 3. Infrared spectrum in the carbonyl stretching region in THF of II after attempted removal of HMPT.

When 1,1,3,3-tetramethylguanidine (pK_a ~ 13.7) was allowed to react with $[Cr_2H(CO)_{10}]^-$ in a small amount of THF, a red-orange solution formed. However, removal of solvent yielded yellow $[Cr_2H(CO)_{10}]^-$. Presumably the guanidine was basic enough to remove the hydrogen as a proton[5] to give the 1,1,3,3-tetramethylguanidinium ion[23] stabilized by $Cr(CO)_5$ moieties.



Under vacuum, the guanidine was lost and the carbonyl complex reverted to $[Cr_2H(CO)_{10}]^-$.

Reduction of $[Cr_2(CO)_{10}]^{2-}$. When either the yellow sodium salt or the tetraethylammonium salt of I was allowed to react with another equivalent of sodium in HMPT, a dark red solution was formed. No CO was evolved if the stoichiometric amount of sodium was added in one portion. When the sodium was added in small portions, some CO evolved, but it never corresponded to a molar equivalent based on I. The excess HMPT was removed by stirring the reaction mixture with petroleum ether. This left a viscous red oil which has the infrared spectrum shown in Figure 2. The spectrum showed three distinct bands almost identical in position with the infrared spectrum of I in HMPT shown in Figure 1b. In water or ethanol the red oil rapidly became yellow. It was extremely sensitive to air. In another experiment, $[(C_2H_5)_4N][Cr(CO)_5Br]$ in HMPT was treated with 2 equiv of sodium. The yellow-orange solution became dark red, and the solution again gave the spectrum shown in Figure 2. This is in contrast to the reaction of $[(C_2H_5)_4N][Cr(CO)_5Br]$ with Na(Hg) in THF where only I was isolated as a product. Any attempt to remove HMPT completely led to a red solid with an infrared spectrum shown in Figure 3. Bands A, B, C, D, and E are characteristic of I as its sodium salt, but the remaining bands, G and H, are new (Table II). These will be explained later. When the crude reaction mixture as a red oil was mixed with tetraethylammonium bromide in ethanol, a yellow solid was isolated, whose infrared spectrum in HMPT was identical with that of I. An infrared spectrum in THF of the evaporated filtrate, which was still red, showed it to consist of a material with bands G and H (Figure 3). The presence of $[Cr_2H(CO)_{10}]^-$ was also noted by infrared[5] and nmr.[5] Evidently the removal of coordinated HMPT encouraged the formation of I and $[Cr_2H(CO)_{10}]^-$.[24]

Table II. Infrared Spectra in the Carbonyl Stretching Region for $[Cr(CO)_5HMPT]^{2-}$ after Partial Removal of HMPT

Band	cm^{-1}	Band	cm^{-1}
A	1903	E	1801
B	1880	G	1842
C	1776	H	1869
D	1756		

We have interpreted these results to mean that the metal-metal bond in I has been cleaved to give $[Cr(CO)_5HMPT]^{2-}$, with the HMPT strongly coordinated to the $Cr(CO)_5$ moiety. Ordinarily one might expect that the addition of another electron to I would give a species with an infrared spectrum in which the stretching frequencies were shifted to longer wavelengths. However, the strongly coordinated HMPT could accept enough electron density to cancel any such change. Wayland and Drago[25] have discussed the coordination of

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[23] P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. I, W. A. Benjamin, Inc., New York, N. Y., 1965, p 277.

[24] Ordinarily the metathesis of I as its sodium salt with tetraethylammonium bromide in ethanol does not display any evidence for $[Cr_2H(CO)_{10}]^-$ when the ethanolic solutions are cold.

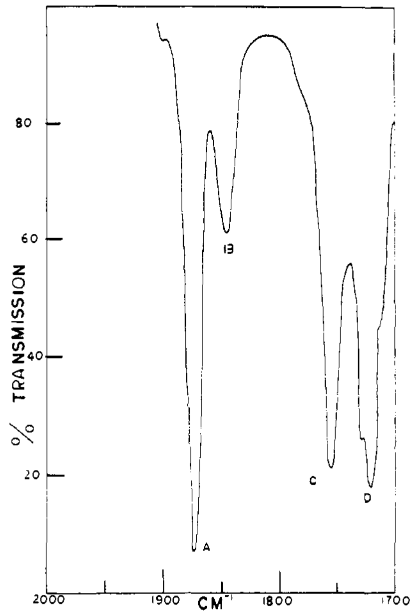
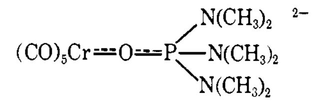


Figure 4. Infrared spectrum in the carbonyl stretching region in HMPT for the product from $Cr(CO)_6$ and Cs(Hg).

HMPT to transition metals and have proposed a model whereby HMPT can delocalize electron density from metal orbitals.



$$\left[(CO)_5Cr{=\!=}O{=\!=}P(N(CH_3)_2)_3\right]^{2-}$$

II

The Effect of Other Reducing Agents. The reaction of $Cr(CO)_6$ with sodium in liquid ammonia[8] in a 1:2 equivalent ratio, respectively, yielded a red solid after removal of the ammonia. Although a portion of the solid was insoluble in THF, an infrared spectrum of the THF-soluble portion showed all the bands reported in Figure 3. Bands G and H dominated the infrared spectrum and hence suggested the presence of another species. Unfortunately we could not separate the compounds associated with these bands.

Chromium hexacarbonyl was reduced with the radical anion of trimesitylboron (TMB),[26,27] which serves only as an electron-transfer species. Removal of the TMB and THF left an orange solid whose infrared spectrum had all the bands shown in Figure 3, except that peaks G and H dominated the spectrum. Even with a large excess of chromium hexacarbonyl the product, after removal of THF, TMB, and chromium hexacarbonyl, had the same infrared spectrum.

In another experiment, phenanthrenesodium was used to reduce chromium hexacarbonyl in THF. Removal of phenanthrene and THF left a brown solid whose infrared spectrum in THF was similar to Figure 3.

In contrast to the foregoing homogeneous reductions, the use of sodium amalgam in boiling THF gave a product whose infrared spectrum was primarily the sodium salt of I. Additional bands were also present and these will be discussed later.

These results mean that bands G and H may be related to II, which suggests that II might have a different configuration in THF. One such configuration for a pentacoordinate structure is a trigonal bipyramid like $Fe(CO)_5$[2b] (ν_{CO}(heptane) 2023, 2000 cm^{-1}). Other pentacoordinate metal carbonyl compounds such as $[Mn(CO)_5]^-$ (ν_{CO} 1863, 1898 cm^{-1}) also have two major carbonyl stretching frequencies[16b] in the infrared. We suggest that bands G and H represent a trigonal-bipyramidal configuration (III) in THF. They related well with CO stretching frequencies in $Fe(CO)_5$ if a shift of 150 cm^{-1} to lower frequencies accounts for the two negative charges. Furthermore the relationship is in the right direction with $[Mn(CO)_5]^-$.

The infrared spectrum of III in THF reverts to the spectrum in Figure 2 upon addition of acetonitrile or HMPT.

Reduction with Potassium and Cesium Amalgam. When 1% potassium amalgam was used to reduce chromium hexacarbonyl in hot THF, a bright green solid was formed, whereas 1% cesium amalgam gave the green product at room temperature in THF. When a large excess of cesium amalgam was used, titration of the remaining amalgam indicated that 4 equiv was utilized. The same green precipitate was obtained by treating the tetraethylammonium salt of I with 1% potassium or cesium amalgam in THF. During this latter reaction, 1 equiv of CO was evolved and 1 equiv of alkali metal was used even though an excess was present. Note that this result is in sharp contrast to the reduction of I with sodium in HMPT in which no CO is evolved. The infrared spectrum of the green solid in acetonitrile or HMPT is shown in Figure 4. The bands C and D are major peaks in the reaction of chromium hexacarbonyl with 2 equiv of phenanthrenesodium besides the other bands which have been mentioned. These same bands occurred in the infrared spectrum of the crude reaction mixture when chromium hexacarbonyl was reduced with sodium in HMPT and sodium amalgam in boiling THF (see also Table III).

In HMPT the green product yielded an orange-red solution from which the original green solid was not recovered. Any attempt to remove the solvent left a material whose infrared spectrum represented a combination of I and II in THF as shown in Figure 3. The previous experiments illustrate that the loss of one carbon monoxide molecule from I leaves a solid which may be formulated as the $[Cr_2(CO)_9]^{4-}$ ion. The

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(25) B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, **87**, 2372 (1965). A referee has suggested that possibly the $[Cr_2(CO)_{10}]^{2-}$ ion is not being reduced, and that perhaps it is the cation or HMPT that is reacting with the solvated electron. We have performed the same reactions with the sodium salt as with the tetraethylammonium salt and have observed no difference. It is possible that the HMPT could be reduced, although there have been differing reports on the stability of the solvated electron in HMPT;[13] *cf.* H. W. Sternberg, R. E. Markby, I. Wender, and D. M. Mohilner, *ibid.*, **89**, 186 (1967), and R. Catterall, L. P. Stodulski, and M. C. R. Symons, *J. Chem. Soc.*, *A*, 437 (1968). One of the products of HMPT cleavage is the dimethylamide anion which is colorless,[13] but we have found no evidence for dimethylamine upon hydrolysis of the reaction mixtures. Since the blue solution of sodium in HMPT was immediately discharged upon addition to a yellow solution of I in HMPT, we have concluded that reaction with I had occurred.

(26) T. L. Chu and T. J. Weismann, *J. Am. Chem. Soc.*, **78**, 23 (1956).

(27) An attempt was made to reduce $Cr(CO)_6$ with $Na_2B_{10}H_{14}$ in THF since $B_{10}H_{14}$ forms radical anions and dianions much like aromatic hydrocarbons; *cf.* E. B. Rupp, D. E. Smith, and D. F. Shriver, *ibid.*, **89**, 5562 (1967). Although reduction does not occur, a pale yellow to light green solid was isolated. The solid was very air sensitive, and infrared spectra showed four bands in the carbonyl stretching region. F. Klanberg and L. J. Guggenberger, *Chem. Commun.*, 1293 (1967), have discussed the structure of NaB_3H_8 adducts with $Cr(CO)_5$. It is conceivable that the higher polyhedral borane adducts may have similar structures.

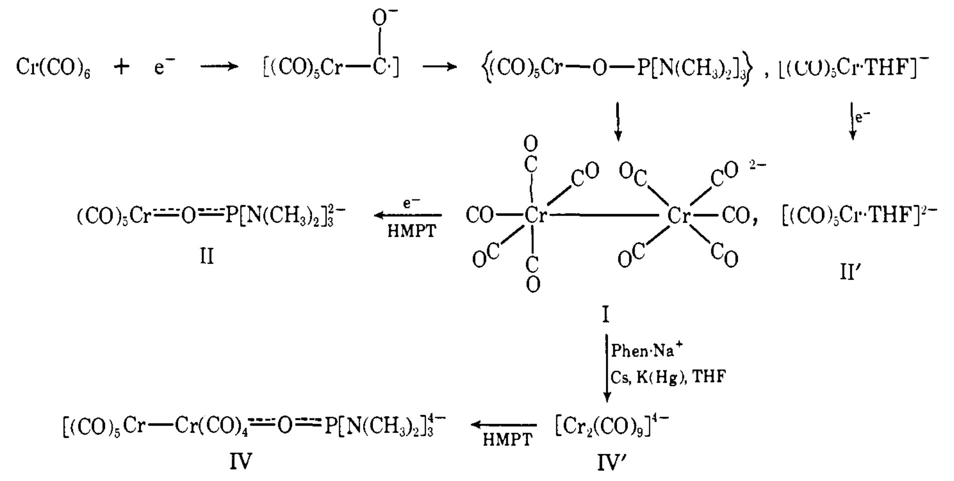
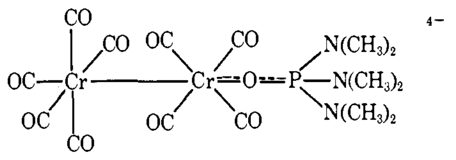


Figure 5. The reduction of chromium hexacarbonyl.

infrared spectrum of this ion in acetonitrile or HMPT may best be described in terms of the following arrangement.



IV

Structure IV should ideally have five infrared-active bands, three from the $Cr(CO)_5$ moiety and two from the $Cr(CO)_4$ portion of the molecule.[28] Bands A, B, and C resemble the spectrum for I except that band B is at 1840 cm^{-1} rather than 1903 cm^{-1} and band C is at 1750 cm^{-1} rather than 1776 cm^{-1}. Band D is not exceptionally well resolved and probably contains more than one absorption. The failure to observe a band at 1903 cm^{-1} in CH_3CN or HMPT solutions of the green solid suggests that II is not present.

Table III. Infrared Spectra in the Carbonyl Stretching Region for $Cs_4Cr_2(CO)_9$ in HMPT (cm^{-1})

Band	cm^{-1}	Band	cm^{-1}
A	1869	C	1750
B	1840	D	1716

The infrared spectra of other compounds such as $[(CO)_5Cr\text{-}Mn(CO)_5]^-$[3b] ($\nu_{CO}$ 2063 (w), 1990 (s), 1950 (ss), 1925 (m), 1896 (s), 1865 (m) cm^{-1}), $[(CO)_5W\text{-}Co(CO)_4]^-$[29] ($\nu_{CO}$ 2062 (w), 2012 (m), 1940 (vs), 1912 (w sh), 1864 (m) cm^{-1}, and $CpMoH_2\text{-}Mo(CO)_5$[30] ($Cp = C_5H_5$) (ν_{CO} 2066 (w) 1937 (s), 1914 (m) cm^{-1}) may be related to IV. If there is relatively little electron delocalization across the metal–metal bond as postulated by Anders and Graham,[3b] then the $Mn(CO)_5$ and $Co(CO)_4$ moieties may tend to accumulate more electron density than the $Cr(CO)_5$ or $W(CO)_5$ moiety. Thus the addition of two more electrons to I to form IV might lead to more electron density on the $Cr(CO)_4L$ moiety in IV. This corresponds to a shift of ~200–250 cm^{-1} [18] to longer wavelengths for some of the bands in I, although it is difficult to predict which bands in I are affected since peak assignments have not been made.

Over-All Reduction. We may now reconstruct the reduction of chromium hexacarbonyl. The first step may be envisaged as the formation of a radical-anion intermediate much the same as an organic ketyl,[31] $[(CO)_5CrCO]^-M^+$. This species rapidly loses CO to form a solvent-stabilized anion which may dimerize to I, if it cannot find another electron, or it may accept an electron, in which case II would be formed. The reduction of chromium hexacarbonyl with sodium amalgam in THF was studied in the infrared cell. The only bands observed during the first 10 min of reaction are shown in Figure 1a. The absence of bands G and H shown in Figure 2 suggests that, at least during the first stages of reaction, $[Cr(CO)_5]^{2-}$ is not being formed, or, if it is being formed, it is rapidly reacting with chromium hexacarbonyl.

$$[Cr(CO)_5]^{2-} + Cr(CO)_6 \xrightarrow{THF} [Cr_2(CO)_{10}]^{2-} + CO$$

When TMB-Na is the reducing agent, the initially formed radical anion may readily accept another electron to form II′ (Figure 5) or cleavage of I may occur. In a separate experiment we observed that no reaction occurred with TMB-Na and the tetraethylammonium salt of I. The presence of II′ probably comes from the homogeneous reduction of a solvated radical ion. With chromium hexacarbonyl and TMB-Na in a 1:2 molar ratio, respectively, chromium hexacarbonyl remained in the reaction mixture. Here the reducing agent prefers to attack carbonyl radical ions rather than chromium hexacarbonyl.

Phenanthrenesodium behaves essentially like an electron-transfer moiety, although its properties as an anion include such reactions as metalation and addition to polar molecules such as CO and CO_2. Hence reduction of $Cr(CO)_6$ with this reagent offers the possibility of the following adducts

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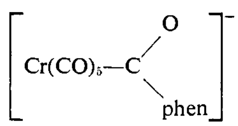
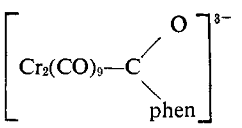
(28) The infrared spectrum of axially substituted $Mn_2(CO)_9L$ has been discussed by M. L. Ziegler, H. Haas, and R. Sheline, *Chem. Ber.*, **98**, 2454 (1965).

(29) J. K. Ruff, *Inorg. Chem.*, 7, 1499 (1968). We appreciate the communication of this work by Dr. Ruff prior to publication.

(30) B. Deubzer and H. D. Kaesz, *J. Am. Chem. Soc.*, **90**, 3276 (1968).

(31) Such a radical anion has been postulated; *cf.* R. E. Dessy, F. E. Stang, R. B. King, and M. Waldrop, *ibid.*, **88**, 471 (1966).





These are analogous to methyllithium adducts of chromium hexacarbonyl observed by Fischer.[32] Attempts to isolate such adducts were unsuccessful as the phenanthrene was recovered quantitatively with no CO present. Nevertheless, the properties of phenanthrenesodium allow for facile removal of CO from chromium hexacarbonyl and its ions. A separate reaction of phenanthrenesodium with the tetraethylammonium salt of I in THF resulted in a green precipitate. This green solid had the same infrared spectrum as shown in Figure 4. Hence, the major reaction was removal of a CO molecule which was not possible when the same reaction was performed with TMB–Na.

The use of more powerful reducing agents such as potassium and cesium amalgam readily cleave CO groups from I. When $[Cr(CO)_5Br]^-$ was allowed to react with potassium or cesium amalgam in THF, a green precipitate formed. The infrared spectrum in HMPT was exactly like that in Figure 4. In addition a moderate amount of chromium hexacarbonyl was found in the vacuum trap. These reactions may be explained by the equations

$$[Cr(CO)_5Br]^- + Cs(Hg) \longrightarrow [Cr_2(CO)_{10}]^{2-}$$

$$[Cr_2(CO)_{10}]^{2-} + Cs(Hg) \longrightarrow [Cr_2(CO)_9]^{4-} + CO$$

Hayter[5] has observed the presence of chromium hexacarbonyl in redox reactions of I. The appearance of chromium hexacarbonyl in the reduction of $[Cr(CO)_5Br]^-$ is not easily explained although it may involve a redistribution of CO groups. These reactions are all cast in perspective with Figure 5.

Experimental Section

Manipulation of Compounds. All operations were performed under argon after several observations that I, which is normally bright yellow, became orange under pure nitrogen. Prepurified argon was passed through four consecutive towers 123 × 2.5 cm. One of the columns contained BTS-Katalysator[33] to remove oxygen, and the remaining towers contained Drierite, Linde 4A Molecular Sieves, and phosphorus pentoxide. The pure gas was transferred to all systems *via* glass, Teflon, and butyl rubber tubing.

A drybox (Vacuum Atmospheres Corp., North Hollywood, Calif. 91605) was used to transfer compounds. The inert atmosphere of the box was circulated through a column of BTS-Katalysator and molecular sieves. Dishes of sodium-potassium alloy and phosphorus pentoxide were always exposed to the inert atmosphere during operations.

Tetrahydrofuran was distilled directly from lithium aluminum hydride into the reaction flask. Chromatographic quality acetonitrile was distilled from calcium hydride. Hexamethylphosphoramide was distilled under vacuum from sodium and triphenylmethane directly into a reaction flask. Ethanol was distilled from calcium hydride and stored over molecular sieves, 4A. Solvents for infrared spectra were stored in the drybox.

Lithium chloride or bromide from Research Organic/Inorganic Chemical Corp. was received in a sealed vial. It was then stirred with anhydrous THF under argon. After removal of the THF, the solid was set under vacuum and heated to 450° for 6 hr. A Nujol mull of the dried salt was prepared in the drybox with Nujol that had been boiled with sodium. An infrared spectrum showed *no* band at 3440 cm^{-1}, the OH stretching frequency for water.

Infrared solutions were prepared in demountable liquid cells with NaCl windows and Teflon spacers. The infrared spectra for most of the compounds were essentially the same with Irtran-2 windows; hence NaCl did not affect the spectra. Amalgam spacers were not used in the demountable liquid cells. The spectra of solids were taken as mulls in Nujol or perfluorokerosene. The infrared spectra were recorded on a Beckman IR-7 (prism grating) instrument, which was calibrated in the 1700–2050-cm^{-1} region with a polystyrene film and atmospheric water vapor.[34] The accuracy is approximately ± 1 cm^{-1}.

Infrared spectra in the carbonyl region were generally recorded at a scan speed of 8 cm^{-1}/min and a slit width of 0.4–0.6 mm.

A. Reaction of Chromium Hexacarbonyl with Sodium in HMPT. To a suspension of 0.50 g (0.00226 mole) of chromium hexacarbonyl in 40 ml of HMPT was added 0.052 g (0.00226 g-atom) of sodium. The reaction mixture was placed under vacuum and the HMPT immediately became yellow. Carbon monoxide was removed under vacuum. Over a 6-hr period all of the sodium dissolved, whereupon the reaction mixture was deep red. The reaction mixture was poured into 400 ml of degassed petroleum ether (bp 30–60°), and a red oil separated.[35] The petroleum ether was decanted from the red oil which was washed three times with degassed petroleum ether. The oil solidified when benzene or ether was added. The resultant red solid was recrystallized from THF–ether to give bright yellow needles of $[Na]_2[Cr_2(CO)_{10}]$, 0.45 g (92.5% yield). A red-brown solid was isolated from the mother liquor. This solid slowly turns green in air and readily dissolves in water with the liberation of gas. The solid dissolves incompletely in HMPT and THF to give yellow solutions whose infrared spectra show bands due to I and II.

B. Reaction of $[(C_2H_5)_4N]_2[Cr_2(CO)_{10}]$ with Sodium in HMPT. A yellow solution of $[Et_4N]_2[Cr_2(CO)_{10}]$ (0.3 g, 0.000466 mole) was treated with 0.0214 g (0.000932 g-atom) of sodium.[36] The solution was stirred magnetically and the sodium slowly dissolved over a 3-hr period to give a bright red solution. The solution was poured into 400 ml of degassed petroleum ether. The red oil readily dissolved in THF to give a bright red solution, whereas $[(C_2H_5)_4N]_2Cr_2(CO)_{10}]$ has limited solubility and may be precipitated by adding THF.

C. Reaction of $Cr(CO)_6$ with Cesium Amalgam. Chromium hexacarbonyl (0.4 g, 0.00181 mole) and cesium amalgam (0.96 g of cesium, 0.0072 g-atom in 7 ml of mercury) were stirred at room temperature in THF. A green precipitate formed in 15 min. In 2 hr considerable green solid had formed. The solid was slurried into another flask, and the cesium amalgam was destroyed with water. Titration of the water solution indicated that 0.0066 equiv of cesium had been used. An infrared spectrum of the THF mother liquor showed bands characteristic of $[Cr_2H(CO)_{10}]^-$. When the green solid was added to water, copious quantities of gas evolved. The green product appeared to react with methylene chloride. In nitromethane it became incandescent and exploded.

The green solid was washed three times with fresh THF. It was heavily contaminated with mercury sludge from the amalgam, and carbon analyses were extremely poor. Cesium was analyzed by first decomposing the solid in water and weighing the mercury. Cesium was determined gravimetrically with sodium tetraphenylboron.[37] *Anal.* Calcd for $Cs_4Cr_2(CO)_9$: Cs, 59.89. Calcd for $Cs_4Cr_2(CO)_9 \cdot C_4H_8O$: Cs, 55.39. Found: 55.72.

D. Reaction of $Cr(CO)_6$ with Phenanthrenesodium. A solution of 0.485 g (0.00272 mole) of phenanthrene in THF was allowed to react with 0.0624 g (0.00272 g-atom) of sodium for 24 hr. Over this period the sodium dissolved to form a deep green solution.

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[32] E. O. Fischer and A. Massbol, *Angew. Chem. Intern. Ed. Engl.*, 3, 580 (1964).

[33] BTS-Katalysator was generously donated by Badische Anilin & Soda-Fabrik Akt.-Ges., Ludwigshafen am Rhein, Germany.

[34] *Pure Appl. Chem.*, **1**, 537 (1961).

[35] When pentane was added to the reaction mixture, the pentane–HMPT layer became bright green. Furthermore, the same green layer was observed to a lesser extent when the reaction mixture was poured into 400 ml of pentane. Removal of pentane left a green oil which slowly became red to red-brown on standing. No green solid could be isolated.

[36] If the sodium was added slowly to the yellow solution, a small amount of gas was evolved, whereas no gas was evolved when the sodium was added in one portion. When the red reaction mixture was added to petroleum ether, the petroleum ether–HMPT layer was sometimes faintly green. Solutions from which the elimination of gas was observed usually yielded HMPT–petroleum ether layers which were decidedly green. No green solid could be isolated from the solutions.

[37] It was virtually impossible to remove the finely powdered mercury completely from the green solid. An infrared spectrum of the solid in perfluorokerosene showed the presence of C–H stretching bands. This suggests that coordinated THF was present in the molecule.

The solution of phenanthrenesodium was poured into a dropping funnel under argon and slowly added to a THF solution of $Cr(CO)_6$ (0.3 g, 0.00136 mole) at room temperature. The green radical anion was immediately discharged upon addition to the chromium hexacarbonyl–THF solution which became yellow. Slowly the solution became dark red-brown. There was little if any gas evolved. Removal of excess THF yielded a rust-red solid. The phenanthrene was recovered quantitatively by washing the rust-red solid with dry benzene. Infrared spectra of this rust-red solid in perfluorokerosene and nmr spectra gave no evidence for phenanthrene.

E. Reaction of $Cr(CO)_6$ with Trimesitylboron Sodium. A solution of trimesitylboron (1.002 g, 0.00272 mole) was allowed to react with a fourfold excess of sodium for 12 hr. The deep blue trimesitylboron sodium was poured completely into a dropping funnel and then added to chromium hexacarbonyl (0.3 g, 0.00136 mole) in THF. The solution became bright yellow to yellow-orange. Dry benzene was used to quantitatively removed trimesitylboron from the reaction mixture after THF had been removed.

F. Reaction of $[Cr(CO)_5Br]^{-}$[38] with Sodium and Potassium Amalgam. A yellow THF solution of $[(C_2H_5)_4N][Cr(CO)_5Br]$ (0.3 g, 0.000746 mole) was treated with sodium amalgam (0.15 g of sodium, 0.00655 g-atom, in 1.1 ml of mercury) at room temperature for 5 hr. No gas evolution was observed. A white-yellow solid formed at 15 min of reaction. The reaction mixture was decanted from the amalgam which was decomposed with water and then titrated with standard acid. A titration indicated that 0.001 equiv of sodium had been used.

The same reaction with potassium amalgam (0.0585 g of potassium, 0.00149 g-atom, in 0.5 ml of mercury) gave a green solid; the evolution of gas was observed throughout the 3-hr reaction. The remaining amalgam was decomposed and the solution titrated with standard acid. The titration indicated that 0.00126 equiv of sodium had been used. Chromium hexacarbonyl was also observed in the vacuum trap after removal of solvent from the reaction mixture.

Acknowledgment. The author is grateful to the Research Committee, University of California, Santa Barbara, Calif., for support of this work and to Professor H. D. Kaesz for some helpful suggestions.

[38] E. W. Abel, *J. Chem. Soc.*, 2068 (1963).

On the Nature of the Spin States in Some Binuclear Iron(III) Complexes

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Abstract: Detailed magnetic, Mössbauer, and spectroscopic studies have been made on a number of binuclear Fe(III) complexes in an effort to determine the spin state for the Fe(III) ions. The over-all data are most consistent with a spin of ${}^{5}/_{2}$ for each iron. An explanation is offered for the presence of a relatively intense electronic absorption band in most of the complexes.

There has been recently a large amount of interest in binuclear complexes of Fe(III),[3-6] especially those showing intramolecular antiferromagnetic exchange coupling between the Fe(III) ions. It is now generally agreed that for those species showing strong coupling (that is, effective moments at 300° of <2.0 per iron) there exists a linear or near-linear oxygen bridge between the two iron atoms. The presence of an oxygen bridge is supported by infrared data,[3-5] and the near-linear nature of the bridge has been established by X-ray data for the two different compounds, a complex of N,N′-ethylenebis(salicylideneiminate) (hereafter, salen)[4] and a complex reported by Curry and Busch[7] of the macrocyclic ligand 2,13-dimethyl-3,6,9-12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene (hereafter, B) which has been studied by Fleischer and Hawkinson[8] and shown to be seven-coordinate.

On the basis of differences in Mössbauer and electronic spectral data for a series of binuclear Fe(III) complexes of 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), 2,2′,2′′-terpyridine (terpy), and salen, we previously suggested[3] that the bipy, phen, and terpy system were best formulated as two interacting $S = {}^{3}/_{2}$ systems, while the salen complexes appeared to be $S = {}^{5}/_{2}$ systems. In particular, the former group of binuclear species exhibit quadrupole splittings in their Mössbauer spectra which are unusually large compared to those normally found for $S = {}^{5}/_{2}$ Fe(III). The same group of compounds shows an electronic absorption around 10,000 cm^{-1} with a molar extinction coefficient of $\sim$7, a value unusually large for the spin-forbidden bands usually observed in high-spin Fe(III). The salen complexes on the other hand exhibit small quadrupole splittings and show no electronic absorption attributable to d–d transitions. The correlation between the quadrupole splittings and the existence of the electronic band, both of which are somewhat unexpected for $S = {}^{5}/_{2}$ systems, thus are circumstantial evidence in favor of an $S = {}^{3}/_{2}$ state for the polyimine complexes, although the evidence is much less than conclusive.

We therefore decided to study further these systems in an effort to obtain more data relevant to the question of the spin state of the iron. First we wanted to measure the magnetic behavior down to lower tempera-

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[5] A. V. Khedekar, J. Lewis, F. E. Mabbs, and H. Weigold, *ibid.*, 1561 (1967).

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[7] J. D. Curry and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 592 (1964).

[8] E. Fleischer and S. Hawkinson, *ibid.*, **89**, 720 (1967).