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The Hexaammine Complexes of the Copper(II) Ion

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The X-ray diffraction patterns, electronic spectra, and electron spin resonance spectra of a number of hexaamminecopper(II) complexes have been examined. The results suggest that the chloride and bromide contain the copper(II) ion in an environment involving a static tetragonal distortion of the six ammonia ligands. The iodide, tetrafluoroborate, and perchlorate involve either a restricted rotation of a static tetragonally distorted hexaamminecopper(II) ion or a dynamic tetragonal distion of this cation (pseudo-rotation).

Introduction

Complexes of the copper(II) cation generally involve a tetragonal distortion[1] of the octahedral environment arising from the six ligands surrounding the copper(II) ion. The possibility of the copper(II) ion forming a regular octahedral stereochemistry, while forbidden on theoretical grounds,[2] can only arise if six equivalent ligands are available for coordination. No example of a copper(II) ion involving a completely regular octahedral coordination has yet been found; but the preparation of cubic complexes having the stoichiometry $Cu(NH_3)_6X_2$ (where $X^- = Br^-$ and I^-) suggests its possible existence in these complexes. This paper reports an examination of a series of hexaamminecopper(II) compounds to determine whether six-coordination does occur and to examine the discrepancy between the reported structures[3] and the predictions of the Jahn–Teller theorem.[2]

Experimental Section

Preparation of Compounds.—The hexaamminecopper(II) complexes were prepared as bright blue powders by the action of liquid ammonia on the starting materials shown in Table I. Ammonia gas was liquefied by passing it into a tube, containing the reactant, surrounded by a Cardice–acetone slurry. Excess ammonia was allowed to evaporate, leaving the hexaammine.

As these compounds readily lose ammonia when exposed to air, all samples were handled under an atmosphere of ammonia; the order of increasing stability with respect to loss of ammonia is: $Cl^- < Br^- < I^- < BF_4^- < ClO_4^-$. Samples for reflectance spectra, X-ray, and esr measurements were ground in a mortar enclosed in a polythene bag, through which a continuous stream of ammonia gas was passed.

Physical Measurements.—Electronic reflectance spectra in the region 4000–40,000 cm^{-1} were measured on a Beckman DK-2A recording spectrophotometer fitted with a standard reflectance attachment. X-Ray powder diffraction patterns were recorded on a 19-cm Debye–Scherrer camera, using Cu Kα radiation (λ 1.5424 A) and 4-hr exposures. Room-temperature electron spin resonance spectra were measured on a Hilger and Watt Microspin spectrometer.

Results

X-Ray Diffraction Patterns.—The types of unit cell and the unit cell dimensions obtained are shown in Table I.

A series of decomposition products of $Cu(NH_3)_6I_2$ was also examined. All materials within the range $Cu(NH_3)_6I_2$–$Cu(NH_3)_{4.8}I_2$ were of face-centered-cubic structure, the *a* value being identical with that for $Cu(NH_3)_6I_2$. Further loss of ammonia from $Cu(NH_3)_{4.8}I_2$ resulted in the loss of the face-centered-cubic structure.

Electronic Reflectance Spectra.—The electronic spectra of all the compounds examined were identical in form, the absorption in the visible region consisting of a broad band with a maximum at approximately 16,000 cm^{-1} and a shoulder at approximately 11,000 cm^{-1} (Table II). No absorption occurred between 4000 and 11,000 cm^{-1} which could be assigned as a d–d transition; no further absorption was observed above 16,000 cm^{-1} before the onset of intense charge-transfer transition at $\approx$30,000 cm^{-1}.

Electron Spin Resonance Spectra.—The *g* values obtained from the spectra of microcrystalline samples, using the method originated by Kneubuhl,[4] are given in Table II.

The isotropic spectrum observed for $Cu(NH_3)_6I_2$ is lost as ammonia is lost from the lattice; the change in the spectrum over the composition range $Cu(NH_3)_6I_2$–$Cu(NH_3)_{4.8}I_2$ is shown in Figure 1. The line shape of the spectrum of the latter compound is characteristic of a copper(II) complex with three unequal *g* values.[4]

Discussion

The analytical results given in Table I confirm the original observation[3] that hexaammine complexes of copper(II) are obtainable and suggest their formulation as $[Cu(NH_3)_6][X_2]$, containing the hexaamminecopper(II) cation. The analysis, by itself, does not rule out their formulation as $(Cu(NH_3)_4X_2]\cdot 2NH_3$ involving a copper(II) ion in a six-coordinate environment, but with a tetragonal distortion arising from nonequivalent ligands.

The copper(II) ion has a 3d^9 electron configuration giving rise to a ^{2}D spectroscopic ground state which is split in an octahedral (O_h) crystal field[5] as shown in Figure 2. The electronic spectrum of a copper(II) ion in a regular octahedral environment should, therefore, consist of a single band, arising from the $^2T_{2g} \leftarrow {}^2E_g$ transition, possibly showing a small splitting due to

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(1) J. D. Dunitz and L. E. Orgel, *Nature*, **179**, 462 (1957).

(2) H. A. Jahn and E. Teller, *Proc. Roy. Soc.* (London), **A101**, 220 (1937).

(3) G. Peyronel, *Gazz. Chim. Ital.*, **71**, 363 (1941).

(4) F. K. Kneubuhl, *J. Chem. Phys.*, **33**, 1074 (1960).

(5) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., London, 1962, p 102.

Table I

Starting Materials, Analytical, and X-Ray Powder Diffraction (A) Results

Compd	Starting material	Analysis for Cu Found	Analysis for Cu Required	Type of unit cell	*a*	*c*	*c/a*
$Cu(NH_3)_6Cl_2$	$CuCl_2$	26.82	26.85	Tetragonal	10.27 ± 0.01	9.42 ± 0.01	0.917
$Cu(NH_3)_6Br_2$	$CuBr_2$	19.48	19.52	Fcc[a]	10.25 ± 0.01		
$Cu(NH_3)_6I_2$	$Cu(NH_3)_4I_2$	15.16	15.18	Fcc	10.78 ± 0.01		
$Cu(NH_3)_6(BF_4)_2$	$Cu(NH_3)_4(BF_4)_2$	18.73	18.72	Fcc	11.16 ± 0.01		
$Cu(NH_3)_6(ClO_4)_2$	$Cu(NH_3)_4(ClO_4)_2$	17.47	17.47	Fcc	11.34 ± 0.01		

[a] Fcc = face-centered cubic.

Table II

Electronic Spectra (cm^{-1}) and Electron Spin Resonance Results

Complex	Electronic spectra				Esr spectra	$g_\perp$	$g_\parallel$	g_i
$Cu(NH_3)_6Cl_2$	11,200 sh	16,400		38,200	Anisotropic	2.060	2.210	
$Cu(NH_3)_6Br_2$	11,000 sh	16,200		36,600	Anisotropic	2.040	2.213	
$Cu(NH_3)_6I_2$	10,500 sh	15,900	35,200	38,500	Isotropic			2.125
$Cu(NH_3)_6(BF_4)_2$	11,000 sh	15,900	31,200	40,000	Isotropic			2.115
$Cu(NH_3)_6(ClO_4)_2$	10,900 sh	15,600	32,500		Isotropic			2.090

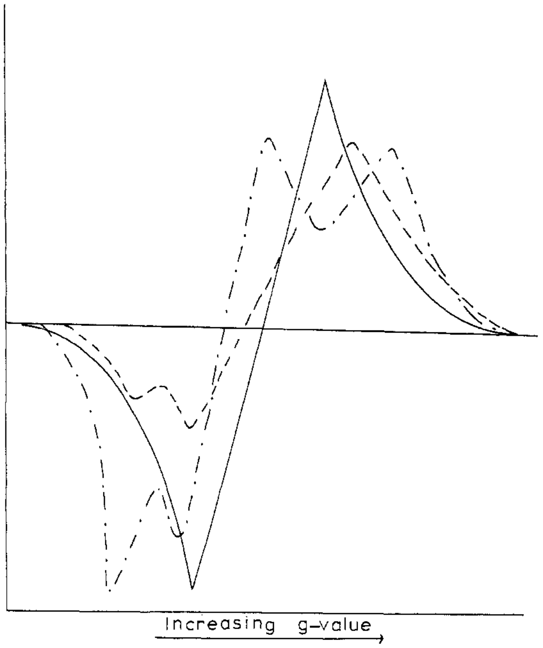

Figure 1.—The effect of decomposition on the first-derivative esr spectrum of hexaamminecopper(II) iodide: ———, $Cu(NH_3)_6I_2$; — —, $Cu(NH_3)_{5.7}I_2$; — · —, $Cu(NH_3)_{4.8}I_2$.

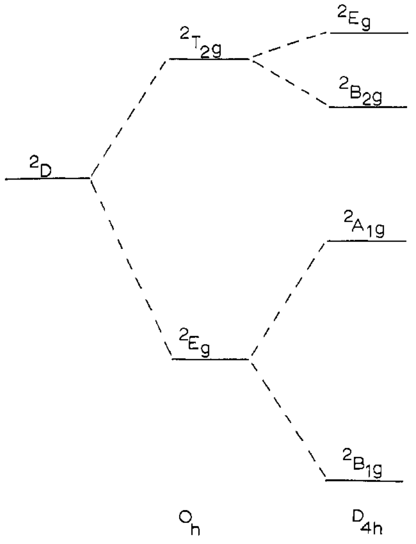

Figure 2.—The splitting of the ^2D spectroscopic term of the copper(II) ion in crystal fields of O_h and D_{4h} symmetry.

spin–orbit coupling.[6] Using the free-ion value of the spin–orbit coupling constant λ of -829 cm^{-1}, this would give rise to a maximum splitting of 1244 cm^{-1}, significantly less than the observed splitting of approximately 5000 cm^{-1}, and rules out a regular static octahedral environment for the copper(II) ion.

The splitting of the ^2D term of the copper(II) ion in a tetragonal crystal field[5] is as shown in Figure 2. As only one region of absorption attributable to d–d transitions is observed, all three transitions probably occur under the envelope of the visible absorption band. The splitting of the ^2E term will be greater than that of the $^2T_{2g}$ term as the ammonia molecule is a predominantly σ-bonding ligand, so the two observed transitions can be tentatively assigned to the $^2A_{1g} \leftarrow {}^2B_{1g}$ and $^2B_{2g}$, $^2E_g \leftarrow {}^2B_{1g}$ transitions. If it is assumed that the splitting of the ^2E_g term obeys a center of gravity rule, the value of $10Dq$ may be calculated as

$$10Dq = E({}^2B_{2g},{}^2E_g \leftarrow {}^2B_{1g}) - {}^1/_2E({}^2A_{1g} \leftarrow {}^2B_{1g})$$

The values of $10Dq$ obtained for Cl^-, Br^-, I^-, ClO_4^-, and BF_4^- are 10,600, 10,700, 10,700, 10,200, and 10,400, respectively. These values are reasonably consistent, and they agree with the reported value of $10Dq$ for hexaamminenickel(II)[7] compounds of 10,750 cm^{-1}; this agreement is some evidence for the validity of the assignment of the electronic spectra of hexaamminecopper(II) compounds as those of tetragonally distorted compounds. The alternative assignment of these spectra to the transitions $^2B_{2g} \leftarrow {}^2B_{1g}$ and $^2E_g \leftarrow {}^2B_{1g}$, with the $^2A_{1g} \leftarrow {}^2B_{1g}$ transition not observed, is not attractive as it implies that the transition $^2A_{1g} \leftarrow {}^2B_{1g}$ is either less than 4000 cm^{-1}, *i.e.*, less than the splitting of the $^2T_{2g}$ (O_h) term, or greater than 30,000 cm^{-1}, an unreasonably large splitting. The possibility

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[6] See ref 5, p 118.

[7] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Ltd., Oxford, 1962, p 123.

that the $^2A_{1g} \leftarrow {}^2B_{1g}$ does occur between 11,000 and 16,000 cm^{-1}, but is so weak that it is not observed, is reasonable, but is considered less likely as it would produce a rather low value of $10Dq$, in the range 9000–6500 cm^{-1}.

Hexaamminecopper(II) bromide is reported to be optically anisotropic;[3] no evidence in support of this statement was found in this work. The electron spin resonance spectra of microcrystalline samples of these hexaammine complexes are given in Table II.

The copper(II) ion in a static tetragonal environment gives rise to an anisotropic esr spectrum, and the expressions for the g values are for a tetragonal environment involving four short and two long bonds (ground state $^2B_{1g}$): $g_{\parallel} = 2[1 - (4\lambda/\Delta)]$ and $g_{\perp} = 2[1 - (\lambda/\Delta)]$.[8] For an environment involving four long and two short bonds (ground state $^2A_{1g}$) the expressions are $g_{\parallel} = 2.0$ and $g_{\perp} = 2[1 - (3\lambda/\Delta)]$.[9] The observed g values for hexaamminecopper(II) chloride and bromide suggest that the copper(II) ion has a $^2B_{1g}$ ground state when the frequency of the principal absorption band (16,000 cm^{-1}) is used for Δ and a value of -500 cm^{-1} for the spin–orbit coupling constant λ. This supports the interpretation of the electronic spectra of these two complexes as suggesting a static tetragonal environment for the copper(II) ions.

The esr spectra of the hexaamminecopper(II) iodide, perchlorate, and tetrafluoroborate are isotropic. An isotropic esr spectrum would only be obtained from a static system if the environment of the copper(II) ion was of regular octahedral symmetry. An isotropic g value[10–12] may also be observed for a copper(II) ion if its otherwise regular octahedral environment is subject to a continuous series of tetragonal distortions in three perpendicular directions (pseudo-rotation). The isotropic g value for a system undergoing pseudo-rotational-type motion is given by the expression[12] $g_i = 2[1 - (2\lambda/\Delta)]$, which, using the above values of Δ and λ, gives $g_i = 2.125$, in reasonable agreement with the observed isotropic g values.

An isotropic esr spectrum would also be produced if tetragonally distorted cations were undergoing free rotation in the crystal lattice, as the rotational frequency could be greater than the frequency of the esr radiation.

Why, in this series of hexaammine complexes, the chloride and bromide should involve static tetragonal environments for the copper(II) ion and yet the iodide, tetrafluoroborate, and perchlorate should involve a pseudo-rotation type of distortion is not understood. The latter are significantly more stable with respect to loss of ammonia and may reflect the stabilizing effect, of the larger anion present, on the lattice energy and hence on the hexaamminecopper(II) cation. In addition, in a static environment four ammonia molecules are strongly bonded and two are very weakly bonded and hence readily lost; in a pseudo-rotational environment all six ammonia molecules must on the average be equally bonded, and the complex will be more stable to loss of ammonia.

The results of the X-ray powder diffraction measurements are shown in Table I; of the hexaamminecopper(II) complexes the chloride was shown to be tetragonal with a c/a ratio <1 and the remainder were shown to be cubic. If the c/a ratio of <1 is taken to reflect directly the local copper(II) ion environment, then this would imply the presence of an environment involving two short and four long copper–ligand distances, which contradicts the results of the esr data which suggested the normal environment of four short and two long distances. Both pieces of evidence can be reconciled if the structure of the chloride involved two normal tetragonal axes mutually at right angles to each other, a structure which is also consistent with the tetragonal electronic spectra.

The unit cell dimensions a of the cubic complexes show an increase in the sequence $Br^- < I^- < BF_4^- < ClO_4^-$ consistent with the increasing size of these anions in this order. The systematic absences in the (hkl) values in the powder patterns of these complexes confirm that they are all face-centered cubic.[13] Peyronel[3] interpreted these results to indicate, for the bromide, that the copper(II) ion must be involved in a regular octahedral coordination. This is not so, as a structure involving three static, tetragonally distorted environments arranged in three mutually perpendicular directions would give a cubic unit cell, an anisotropic g value, and a tetragonal electronic spectrum and is the structure suggested for hexaamminecopper(II) bromide. This type of lattice has been reported for β-$Cu(NH_3)_2Cl_2$ and β-$Cu(NH_3)_2Br_2$.[14]

The line intensity calculations of Peyronel[3] strongly suggest that this cubic hexaammine is best formulated as $Cu(NH_3)_6Br_2$ involving the hexaamminecopper(II) cation but does not completely rule out the possible formulation of this complex as $[Cu(NH_3)_4Br_2]\cdot 2NH_3$. The observation that hexaamminenickel(II) bromide is isomorphous with the copper complex,[15] both in line index and line intensity, makes the formulation of these complexes as tetraammines highly unlikely. The nickel(II) ion is likely to prefer the formation of a regular six-coordinate cation $Ni(NH_3)_6^{2+}$ rather than the tetragonally distorted structure $Ni(NH_3)_4Br_2$ in which the bromide ions have displaced two ammonia ligands from the nickel ion environment in contradiction to their respective positions in the spectrochemical series.[16] In addition, the reflectance spectrum of hexaamminenickel(II) bromide has a first ligand field band at 10,800 cm^{-1} consistent with an absorption at 10,750 cm^{-1},[7] for the hexaamminenickel(II) anion in aqueous ammonia solution, where the nickel ion is certainly in-

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[8] D. Polder, *Physica*, **9**, 709 (1942).

[9] See ref 5, p 134.

[10] J. H. Van Vleck, *J. Chem. Phys.*, **7**, 61 (1939).

[11] U. Opik and M. H. L. Pryce, *Proc. Roy. Soc.* (London), **A238**, 425 (1957).

[12] A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **3**, 304 (1958).

[13] R. W. M. D'Eye and E. Wait, "X-Ray Powder Photography in Inorganic Chemistry," Butterworth and Co. Ltd., London, 1960, p 81.

[14] F. Hanic and J. Cakajdova, *Acta Cryst.*, **11**, 610 (1958).

[15] G. Bodtker-Raess and O. Hassel, *Z. Physik. Chem.*, **B22**, 471 (1933).

[16] See ref 7, p 107.

volved in sixfold coordination with respect to ammonia nitrogens. Assuming the law of average environment to apply, the complex $[Ni(NH_3)_4Br_2]\cdot 2NH_3$ should give a first ligand-field band at 9500 cm^{-1}, a difference which would be clearly detectable in the reflectance spectrum.

The cubic unit cell dimensions of the hexaamminecopper(II) iodide, perchlorate, and tetrafluoroborate, if they involve pseudo-rotation, are also understandable as their measurement by the relatively slow process of X-ray diffraction will yield a time-average structure. The process involved in measuring an electronic spectrum are fast, relative to the frequency of pseudo-rotation, and the electronic spectrum will reflect the distorted configuration in which the system spends the most time. Thus, the cubic structures, tetragonal electronic spectra, and isotropic esr spectra observed for $Cu(NH_3)_6I_2$, $Cu(NH_3)_6(BF_4)_2$, and $Cu(NH_3)_6(ClO_4)_2$ are consistent with hexaamminecopper(II) cations undergoing pseudo-rotational motion.[12]

As a cubic unit cell is observed for all compounds in the composition range $Cu(NH_3)_6I_2$–$Cu(NH_3)_{4.8}I_2$, evidence on the coordination of the copper(II) ion cannot be obtained from the X-ray diffraction data alone. However, in this system an isotropic g value is only obtained for the compound of composition $Cu(NH_3)_6I_2$, the observed esr spectra becoming increasingly anisotropic as ammonia is lost from the lattice. As an isotropic g value (in a magnetically dilute system) can only arise from a copper(II) ion surrounded by six equivalent ligands, all six ammonia molecules in hexaamminecopper(II) iodide must be coordinated to the copper(II) ion. The immediate change in the esr spectrum as ammonia is lost from the lattice is probably the result of ammonia molecules being lost randomly from the coordination spheres of the copper(II) ions. As the lattice consists of close-packed halide ions with the hexaamminecopper(II) cations in the octahedral holes, a considerable amount of ammonia may be lost in this way before the lattice becomes distorted.

The observation of a cubic unit cell does not rule out the possibility that these complexes contain a freely rotating, tetragonally distorted copper(II) ion environment, as the time-average structure would be cubic. However, the volume swept out by a rotating, distorted cation would be greater than the volume of a static, octahedral cation, so the apparent unit cell dimension would be greater. The unit cell dimensions of the isostructural compounds of the other divalent ions of the first transition series are compared in Table III.

TABLE III
THE UNIT CELL DIMENSIONS OF HEXAAMMINEMETAL(II) COMPLEXES (A)[a]

	Br^-	I^-	BF_4^-	ClO_4^-
Ca	10.71	11.24		
Mn	10.52	11.04		
Fe	10.47	10.97		
Co	10.39	10.91	11.31	11.45
Ni	10.34	10.88	11.27	11.41
Cu	10.25	10.78	11.16	11.34
Zn	10.46	10.96		

[a] Data from ref 15, except for copper(II).

As ammonia is a relatively weak ligand,[7] it forms high-spin complexes with the divalent transition metal ions in these octahedral complexes. The variation in cationic size predicted by ligand-field theory is, therefore, Mn > Fe > Co > Ni > Cu < Zn.[17] Thus, an octahedral hexaamminecopper(II) cation is expected to be larger than a hexaamminenickel(II) cation, and, if free rotation is occurring in the copper(II) compounds under examination, this increase in size should be accentuated. If the variation of the unit cell dimensions is taken as a measure of the variation of the cationic sizes, all of the hexaamminecopper(II) cations in Table III are smaller than the corresponding hexaamminenickel(II) cations, which is evidence against the occurrence of free rotation of tetragonally distorted cations in the copper(II) compounds. While free rotation of a tetragonally distorted copper(II) cation is ruled out, a more restricted rotation of a given tetragonal unit, randomly about the three perpendicular cartesian directions, is possible. If the rotation is fast enough, this will produce an isotropic g value and will, if certain geometrical requirements are fulfilled, result in a reduction of the unit cell parameter below that of the corresponding nickel complex. Assuming that the copper(II) ion could occupy a regular octahedral environment, then ligand-field theory would predict that the unit cell parameter $\bar{a}$ for the hexaamminecopper(II) iodide would be 10.92 A, the mean of the values for the corresponding nickel and zinc complexes. Using a Pauling ionic radius of 2.16 A for the iodide ion and an N–H bond length of 1.34 A as in the ammonium cation,[18] assuming a tetragonal Cu–N–H bond angle, free rotation of the ammonia groups about the copper–nitrogen bond, and that the plane of the three terminal hydrogen atoms on any one ammonia group contains the lines joining the centers of the adjacent iodide ions, then an estimated copper–nitrogen distance of 2.30 A is obtained. If the copper–nitrogen distance, in this unfavorable octahedral environment, underwent a contraction of 0.25 A in the x and y directions to a copper–nitrogen distance of 2.05 A (as in tetraamminecopper(II) sulfate monohydrate[19]) and an expansion in the z direction to 2.58 A, then these changes would allow a general contraction of the iodide–iodide distances and hence in the unit cell dimension. If the orientation of this static distortion occurred randomly through the lattice and a random restricted rotation about the three cartesian directions occurred, then a cubic unit cell would be retained.

The occurrence of pseudo-rotation of the hexaamminecopper(II) cations would require a unit cell dimension consistent with the predictions of the ligand-field theory,[17] *i.e.*, larger than that of the corresponding nickel complex. The observation of lower unit cell

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(17) J. H. van Santen and J. S. Wieringen, *Rec. Trav. Chim.*, **71**, 402 (1952); L. E. Orgel, *J. Chem. Soc.*, 4756 (1952).

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dimensions for the copper(II) complex would, therefore, question the occurrence of pseudo-rotation alone in these complexes. A closer examination of the process of pseudo-rotation, in the light of these conclusions, confirms that a reduction in the unit cell dimension cannot occur as the movement of the separate ammonia groups is such that at some stage they must separately pass through the position corresponding to a regular octahedral coordination of the copper(II) ion. At this point a general expansion of the interiodide distances must occur for the four iodide ions (which lie in the plane of the ammonia molecule), with a corresponding increase of the unit cell in this plane to 10.92 A, the value applying to a regular octahedral coordination of the copper(II) ion. The only way in which the cubic unit cell could be maintained would be if the expansion in the sheets of iodide ions occurred successively in three planes at right angles and was synchronized to the pseudo-rotation of the hexaamminecopper(II) cations. This situation of coupled pseudo-rotation would produce a slight contraction of the unit cell dimension but is considered less likely than the form of restricted rotation suggested above.

An examination of the effect of temperature on these isotropic esr spectra is in hand in an attempt to resolve these two possible interpretations.

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Reactions of Cyclopentadienyl(methyl)iron Dicarbonyl with Various Ligands. Cyclopentadienyl(acetyl)iron Carbonyl Phosphine and Phosphite Complexes

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Cyclopentadienyl(methyl)iron dicarbonyl reacts with $P(C_6H_5)_3$, $P(n\text{-}C_4H_9)_3$, $P(OC_6H_5)_3$, and $P(OC_4H_9)_3$ in refluxing tetrahydrofuran to give almost quantitative yields of the complexes $C_5H_5Fe(CO)(COCH_3)L$ (L = phosphine or phosphite). The properties of these derivatives are listed, and the infrared and nuclear magnetic resonance spectra are briefly discussed. Under similar experimental conditions there is no reaction between $C_5H_5Fe(CO)_2CH_3$ and diethyl sulfide, iodide ion, *p*-toluidine, and *p*-chloroaniline; pyridine affords a noncarbonyl decomposition product. Furthermore, in contrast to its behavior in tetrahydrofuran, $C_5H_5Fe(CO)_2CH_3$ does not react with triphenylphosphine in refluxing hexane.

Introduction

Recently we have reported that $C_5H_5Fe(CO)_2CH_3$ reacts rapidly with liquid sulfur dioxide[1] and more slowly with SO_2 in pentane[2] to yield the sulfonyl derivative, $C_5H_5Fe(CO)_2SO_2CH_3$. Mechanistically, this "insertion" most likely involves methyl group migration;[3] therefore, particular interest attaches to the fact that the CH_3 becomes ultimately bonded to the attacking SO_2 rather than to a CO present in the complex. Since formation of an intermediate acetyl, $C_5H_5Fe(CO)(COCH_3)SO_2$, cannot be ruled out from the evidence on hand, studies on reactions of $C_5H_5Fe(CO)_2CH_3$ with nucleophiles onto which the methyl group cannot migrate may provide valuable information concerning the course of the sulfur dioxide "insertion."

Survey of the literature reveals that the only ligand known to react with $C_5H_5Fe(CO)_2CH_3$ to give a cyclopentadienyliron carbonyl acetyl derivative is carbon monoxide.[4] This scarcity of data on $C_5H_5Fe(CO)_2CH_3$ is in contrast to the amount of information available on reactions between $CH_3Mn(CO)_5$ and various nucleophiles. The latter alkyl reacts with carbon monoxide,[5] amines,[6] phosphines, phosphites,[7,8] arsines, stibines,[8] and iodide, cyanide, thiocyanate, and methoxide ions[9] to cause methyl group migration onto a carbonyl ligand.

Our current studies on the mechanism of sulfur dioxide insertion with $C_5H_5Fe(CO)_2CH_3$ prompted us to investigate the reaction of this alkyl complex with several other nucleophiles. It was of particular interest to determine whether, as with $CH_3Mn(CO)_5$, methyl migration is a fairly general reaction and, if so, what properties of a nucleophile are responsible for effecting this process. Reported now are results on reactions of

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