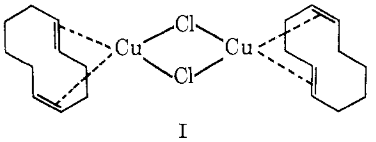
Although no definite structures can be assigned without X-ray data, some general correlation can be drawn from the infrared spectra of these complexes and those of similar complexes whose crystal structures have been determined.

The generally accepted Dewar[13] concept of π bonding appears applicable to the silver(I) and copper(I) cyclodecadiene complexes. The double bond frequencies of the silver(I)–1,5-diene complex have been lowered from two peaks of equal intensity at 1667 and 1639 cm.$^{-1}$ to a weak band from 1660 to 1600 cm.$^{-1}$. A similar change is noted in the 1,6-diene complex, in line with the Dewar concept's prediction that the double bonds of the olefin should not be changed significantly in π complexing with the silver(I) ion.

For both isomers of the 1:1 cyclodecadiene–silver nitrate complexes two possible structures may be proposed. One would be a polymeric structure where the silver ions are associated with two double bonds each from a different olefin molecule. In the other the silver ion is located approximately in the center of the olefin molecule, the cyclic olefin being in a boat configuration with the metal π-bonded to both pairs of double bonds, similar to the arrangement found in the 1:1 cyclooctatetraene–silver nitrate complex.[14]

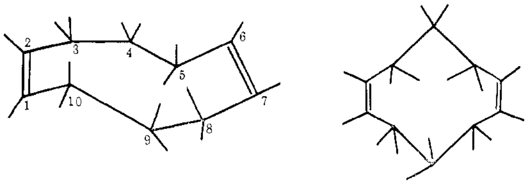
The spectra of all the copper(I) complexes are similar and indicate a π-bonded complex analogous to the silver(I) complexes. The double bond absorption bands characteristic of *cis,trans*-cyclodeca-1,5-diene at 1667, 1669 cm.$^{-1}$ and of *cis,cis*-cyclodeca-1,6-diene at 1675, 1655 cm.$^{-1}$ are absent. A new band at 1613 cm.$^{-1}$ appears which has been assigned to the complexed olefin. The bands in the 1300–650 cm.$^{-1}$ region of the copper(I) complexes are identical with those of the uncomplexed olefins. This seems to indicate no changes in the skeletal vibrations of the C_{10} ring or in the structural conformation of the olefin.

Recent studies by van den Hende and Baird[15] on the structure of cycloocta-1,5-diene–copper(I) chloride indicate this complex to be a chloride-bridged dimer with the copper ion quasi-tetrahedrally bonded to two chloride ions and the two double bonds of the olefin molecule. A similar structure could be postulated for the 1:1 cyclodeca-1,5-diene–copper(I) chloride complex (I). The 1:2 cyclodecadiene–copper(I) bromide complex, on the other hand, is apparently polymeric with bromide bridging groups.



I

Both chair and boat structural conformation of the cyclodeca-1,6-diene molecule are possible (II). Structural models of the chair conformation indicate a high degree of transannular strain from intraannular interactions of the hydrogen atoms on carbons 3, 4, 9, and 10. The boat conformation has interactions of the hydrogen atoms of carbons 3, 5, 8, and 10, but these can be relieved somewhat by a staggered arrangement of the atoms. If the boat form is the preferred conformation, a 1:1 complex should exist. Such a complex would be similar in structure to the 1,5-diene–copper(I) chloride complex. At this time, we have been able to prepare only the 1:2 cyclodeca-1,6-diene–copper(I) halide complex. Therefore, it is not as yet possible to make any statement as to which conformation is preferred. Work with other metal ions is in progress and will be reported shortly.



Chair conformation Boat conformation

II

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[15] J. H. van den Hende and W. C. Baird, *J. Am. Chem. Soc.*, **85**, 1009 (1963).

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The Kinetics of Exchange of Thiocyanate between Iron(III)–Thiocyanate Complexes and Free Ligand in Concentrated Aqueous Solution[1]

BY HAROLD W. DODGEN, ROBERT MURRAY, AND JOHN P. HUNT[2]

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The work reported here is a continuation of studies on thiocyanate complexes. Results were reported earlier for the Ni(II) system[3] while here we are concerned with Fe(III) complexes.

Experimental

The general procedures and equipment have been described.[3] Solutions were prepared using redistilled water and analytical grade reagents (KNCS, HNO_3, and $Fe(NO_3)_3 \cdot 9H_2O$). The Fe(III)–thiocyanate solutions decomposed slowly and extrapolations of the line width data to "zero time" were made when necessary.

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[2] To whom inquiries may be addressed.

[3] R. Murray, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **3**, 1576 (1964).

TABLE I

LINE BROADENING DATA FOR Fe(III)–8.5 M KNCS SOLUTION

Fe(III), M	t, °C.	Δ', gauss	$T'_{2p} \times 10^5$ M sec.
0.05	2.0	0.46	11.2
0.05	15.0	1.38	3.74
0.05	28.0	2.44	2.12[a]
0.03	12.3	0.57	5.44
0.03	21.3	1.03	3.01
0.03	26.0	1.47	2.11[b]
0.03	31.0	1.96	1.58[c]
0.015	28.0	0.87	1.77[d]
0.015	38.5	1.41	1.10

[a] pH 1.02. [b] pH 1.28. [c] pH 2.42. [d] pH 1.24.

Treatment of Data and Results

We have followed the treatment given earlier.[3] We have defined T'_{2p} by $T'_{2p} \equiv 2[\text{Fe(III)}]/\gamma\Delta'$ where [Fe(III)] refers to total iron molarity, γ is the magnetogyric ratio for N^{14} (1934 gauss^{-1} sec.$^{-1}$), and Δ' is the line broadening (in gauss) in free thiocyanate ion, measured from full widths at half-maximum absorption. The results obtained correspond to the case $T'_{2p} = [\text{Fe(III)}]p_0\tau_{40}/p_4$, where p_0 and p_4 are the atom fractions of N^{14} in free and bound thiocyanate, respectively, and τ_{40} is the mean lifetime of a thiocyanate ion for change from the complex to free thiocyanate. No direct measurements on species in thiocyanate solutions at 8 M appear to have been made. Although much study has been given to the question of the species present in Fe(III)–thiocyanate solutions, no clear-cut results are available on the higher species. We have assumed the species $Fe(NCS)_4^-$ to predominate and have calculated our data on this basis. Jørgensen[4] indicates that the iron is bound to sulfur in such species. Our results are not unambiguous on this point but suggest rather that it is the nitrogen atom which is bound to iron. If the thiocyanate ligand is bound to sulfur, then the paramagnetic electrons of iron(III) must be σ delocalized through the SCN linkages. We have found for the Ni(II)–N_3^- system that while the N^{14} line for the terminal atoms in N_3^- is readily broadened by Ni(II), the line for the central nitrogen atom requires about a tenfold greater nickel concentration to produce a broadening effect. This suggests that the σ delocalization in the electronically related azide ion is not very great.

We have arbitrarily used the rate law $R = 4k_1[\text{Fe(III)}]$. The value of k_1 is then given by $k_1 = [\text{NCS}^-]/4T'_{2p}$. Our results are presented in Table I. No large variation in pH was attempted. At low pH the decomposition of thiocyanate becomes a problem; at high pH hydrolysis of Fe(III) will occur. In the range studied (1–2.4) no effects were found. The rate is found to be first order in Fe(III) concentration. We have not varied the thiocyanate concentration in these studies because our experience has shown that it is very difficult to treat the results of such variations considering uncertainties in species and the effects of including several species in the n.m.r. theory. The following rate parameters were calculated: k_1 (25°) = $1.0 \pm 0.1 \times 10^5$ sec.$^{-1}$, $\Delta H^* = 10.3 \pm 0.5$ kcal./mole, and ΔS^* (from k_1) = -1.5 ± 1.5 e.u.

It may be noted here that addition of 0.01 M Fe(II) to 8.5 M KNCS produced no observable line broadening at 27 and 40°.

Discussion

Some data for related systems are given in Table II. As has been noted before, the exchange rate for higher complexes is greater than for the mono complex. The exchange of thiocyanate ion in our case is much more rapid at 25° than water exchange in the aquo Fe(III) ion. The Fe(III) and Ni(II) thiocyanate exchanges have fairly similar apparent rate parameters. Uncertainty as to species makes it difficult to try to understand this result.

TABLE II

RATE DATA FOR LABILE COMPLEXES AT 25°

	k_1, sec.$^{-1}$	ΔH^*, kcal. mole^{-1}	ΔS^*, e.u.	Ref.
$Fe(NCS)_4^- + NCS^- \rightleftharpoons$	$1.0 \pm 0.1 \times 10^5$	10.3 ± 0.5	-1.5 ± 1.5	This work
$Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons$	3×10^3	...	...	a
$Fe(H_2O)_6^{3+} + NCS^- \rightarrow FeNCS^{2+}$	127 (M^{-1} sec.$^{-1}$)	13	−5	b
$Fe(H_2O)_6^{3+} + Cl^- \rightarrow FeCl^{2+}$	9 (M^{-1} sec.$^{-1}$)	17	2	c
$Ni(NCS)_4^{2-} + NCS^- \rightleftharpoons$	7×10^5	9	−5	3

[a] Private communication from R. E. Connick. [b] J. F. Below, Jr., R. E. Connick, and C. P. Coppel, *J. Am. Chem. Soc.*, **80**, 2961 (1958). [c] R. E. Connick and C. P. Coppel, *ibid.*, **81**, 6389 (1959).

It will be of interest to compare the water exchange rate with that for thiocyanate ion in solutions containing the thiocyanate complexes as was done for the nickel system.[3]

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[4] C. K. Jørgensen, "Inorganic Complexes," Academic Press, New York, N. Y., 1963, p. 79.

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The Evaluation of Group Overlap Integrals

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The semi-empirical molecular orbital theory of inorganic molecules,[1] in which there has recently been

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