the slit, then the sample was introduced into the cell by warming the side arm. It took about 2–3 min for the beam power to reach a steady level. Then the side arm was again frozen to restore the power rapidly to the level of the empty cell. The results of the absorption measurements are given in Table I. Experimental uncertainties are $\pm 1\%$ unless otherwise stated. At 400 cm^{-1}, we are already observing the tail portion of the 520-cm^{-1} absorption. It is clear from Table I that the bending mode of XeF_6 must be quite different from those of other known hexafluorides, whose f_{1u} bending modes are sharp and absorption widths at the half-intensity height are normally less than 25 cm^{-1} at the pressure range of 20 mm. Furthermore, the P–Q–R branches are often well resolved at this pressure.

TABLE I

XeF_6 ABSORPTION IN FAR-INFRARED REGION

Freq, cm^{-1}	% power absorption	Freq, cm^{-1}	% power absorption
50	0 ± 3	175	11
75	1 ± 1	200	11
100	4	225	11
125	5	250	13
150	7	400	20

The millimeter wave spectrometer used for this study uses the principle of the free-space cell.[13] The cell is a nickel tube with a 2.5-in. inside diameter and a 5-ft length, with Teflon windows on the ends. The cell was seasoned with ClF_3 and then with XeF_6. The XeF_6 sample stored in the cell was transferred to an infrared cell several times during the investigation and spectra were taken to determine the purity of the sample. Only a small trace of $XeOF_4$ was observed as an impurity. We searched for millimeter wave absorption at room temperature with sample pressures ranging from 50 to 100 μ. The spectral region of 3.7–8.6 cm^{-1} was covered with the fourth, fifth, sixth, and seventh harmonics of the Oki klystrons, 35VII and 30VII. We have not observed any absorption line that can be attributed to the molecule XeF_6.

It is difficult to calculate or even predict the magnitude of the absorption coefficients of the inversion lines embodied in the Bartell model.[9] The sensitivity of the spectrometer is in the range of detecting a line with absorption coefficient greater than 10^{-5} cm^{-1}. The video detection method used sets an upper limit of 15 Mc for the width of absorption line to be detected. With this spectrometer we observed the $J \cong 15$ rotational transitions of XeO_3 with the K components resolved. The XeO_3 spectrum was taken at an elevated temperature of about 100°, and the concentration of XeO_3 vapor was estimated to be not more than a few per cent.

In summary, in the bond-stretching region, distinct infrared bands are observed and there are more than one would expect for O_h symmetry. In the bond-stretching region, however, no definite absorption

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bands can be located. Further, no microwave absorption could be detected in the range 3.7–8.6 cm^{-1}.

These results seem to support either a model that is very nonrigid with respect to angles between bonds or a model of more rigidity but with unusually large anharmonicities in the bending potential function. The anharmonicities are particularly important for such a molecule because of the many low-lying vibrational energy levels. Calculation of Boltzmann distributions, using rough estimates of 200 cm^{-1} for all three triply degenerated bending modes and 600 cm^{-1} for the stretching fundamentals, shows that less than 1% of the molecules at room temperature are in the vibrational ground state. There are 15 excited states for which the populations are comparable to that in the ground state. Thus the spectral features should broaden markedly owing to anharmonicities.

Our results, on the other hand, do not give any support to Bartell's inverting or pseudo-rotator model.[9] Since the results are negative, they cannot definitely rule it out. When the inverting model is taken to parallel that of a rotating diatomic molecule with $B = 3$ cm^{-1} as suggested, an upper limit to the magnitude of the transition dipole moment can be set. Assuming the same values for the vibrational fundamentals as above except the f_{1u} bending mode which transforms to the pseudo-rotation mode, the calculated value of the upper limit[14] is about 0.1 D.

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Infrared Spectra of Copper Thiocyanate Complexes

BY R. H. TOENISKOETTER[1] AND STANLEY SOLOMON

In metal ion compounds the linear thiocyanate ion can coordinate through either the sulfur or the nitrogen atoms, or both.[2] Examples of complexes containing each type of bonded thiocyanate group are known but in general the compounds with first-row transition metals are known to be N-bonded from X-ray data.[3,4] Criteria for establishing the mode of bonding in thiocyanate complexes have been worked out based on the frequency ranges found for the three vibrational modes of the thiocyanate ion, *i.e.*, the C–N[5] and C–S[6–8] stretching modes $\nu(CN)$ and ν

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(CS) and the degenerate bending mode δ(NCS).[8-10] For compounds containing S-bonded thiocyanate ion, a further diagnosis based on the position of the C–N stretching frequency has been used to determine whether bridging of the thiocyanate group exists.[11] For soluble compounds, integrated intensity measurements of ν(CN) provide an excellent tool for study of the mode of bonding in thiocyanate complexes.[12]

During the course of examining several complexes of N-heterocyclic amines with copper(I) and copper(II) thiocyanates, it became evident that the spectral properties due to the thiocyanate group provided an obvious distinction between the mono- and the divalent copper compounds. Thus the copper(I) complexes all appeared to be S bonded whereas the copper(II) compounds contained N-bonded isothiocyanate groups. Additional compounds were prepared, their spectra were recorded, and the results have been correlated with current concepts regarding the nature of the bonding in metal ion complexes.

Results and Discussion

The compounds prepared and their analytical characterization are listed in Table I. Unusual

Infrared spectra were recorded from 5000 to 300 cm^{-1} and all of the complexes exhibited bands characteristic of and very close in position to those of the free organic ligands. Since detailed analyses of the ligand spectra have been reported for related compounds,[13] these general spectral properties are not of concern here. However, some additional comment is in order regarding the pyrazine and piperazine complexes. Although the pyrazine complex with copper(I) thiocyanate appeared to contain bridging pyrazine ligands as evidenced by the absence of absorption bands in the 1030–800-cm^{-1} region,[14] weak bands at 970 and 925 cm^{-1} in the spectrum of copper(II) thiocyanate–pyrazine suggested the occurrence of terminal ligands in this compound. In both piperazine compounds, bands were found between 980 and 1090 cm^{-1} indicating the boat conformation[15] and suggesting that the piperazine molecule functions as a chelating ligand in these complexes. Significant differences also were noted for the spectra of the copper(I) and copper(II) piperazine complexes between 850 and 1150 cm^{-1}. The copper(I) thiocyanate piperazine showed medium strong bands at 860, 982, 998, 1049, and 1087 cm^{-1}. In the copper(II) complex,

TABLE I

DATA FOR COPPER(I) AND COPPER(II) THIOCYANATE COMPLEXES

Complex	Ligand	Color	Mp, °C	%calcd Cu	C	H	N	S	%found Cu	C	H	N	S
CuSCNC$_5$H$_5$N	Pyridine	White	Dec	31.6	35.9	2.51	14.0	16.0	31.1	36.0	2.49	13.7	16.0
CuSCNCH$_3$C$_5$H$_4$N	α-Picoline	White	320 dec	29.6	39.1	3.27	13.1	14.9	29.7	38.4	3.79	13.0	15.3
CuSCNCH$_3$C$_5$H$_4$N	γ-Picoline	White	150 dec	29.6	39.1	3.27	13.1	14.9	30.4	38.4	3.21	12.9	15.4
CuSCN(CH$_3$)$_2$C$_5$H$_3$N	3,5-Lutidine	White	Dec	27.8	42.0	3.96	12.3	14.0	29.1	40.1	3.85	11.8	14.9
CuSCNC$_9$H$_7$N	Quinoline	Yellow	172	25.3	47.9	2.81	11.2	12.8	25.6	47.3	2.70	12.3	13.2
(CuSCN)$_4$(C$_5$H$_{11}$N)$_3$	Piperidine	White	100 dec	34.2	30.7	4.48	13.3	17.3	34.3	30.1	4.52	13.0	17.4
(CuSCN)$_2$(C$_4$H$_{10}$N$_2$)	Piperazine	White	236	38.6	21.9	3.06	17.1	19.4	38.0	22.0	3.17	16.9	19.5
(CuSCN)$_4$(C$_4$H$_4$N$_2$)$_3$	Pyrazine	Yellow-orange	300 dec	34.9	26.4	1.66	19.3	17.6	34.7	26.3	1.77	19.2	17.6
(CuSCN)$_6$(C$_{10}$H$_8$N$_2$)$_5$	2,2'-Bipyridine	Orange	222 dec	25.2	44.5	2.67	14.9	12.7	24.6	44.1	2.79	14.6	12.3
Cu(SCN)$_2$(C$_5$H$_5$N)$_2$	Pyridine	Green	181 dec	18.8	42.7	2.98	16.6	19.0	...	43.0	3.05	17.3	...
Cu(SCN)$_2$(CH$_3$C$_5$H$_4$N)$_2$	β-Picoline	Green	141	17.4	46.0	3.86	15.3	17.5	18.1	45.1	3.69	15.4	17.2
Cu(SCN)$_2$(CH$_3$C$_5$H$_4$N)$_2$	γ-Picoline	Green	124	17.4	46.0	3.86	15.3	17.5	17.3	45.7	3.60	16.1	17.1
Cu(SCN)$_2$C$_4$H$_4$N$_2$	Pyrazine	Yellow-green	350 dec	24.4	27.7	1.55	21.6	24.7	25.0	27.1	1.60	21.7	...
Cu(SCN)$_2$(C$_{10}$H$_8$N$_2$)$_2$	2,2'-Bipyridine	Green	197	12.9	53.7	3.28	17.1	13.0	12.6	52.9	3.28	17.3	13.2

stoichiometries were found for the piperidine, pyrazine, and bipyridine complexes with copper(I) thiocyanate, but these appeared to represent true compound compositions since they were invariant to temperature change in the preparative procedure. Preparation of a pure piperazine complex of copper(II) thiocyanate could not be achieved because of a marked tendency of the compound to undergo reduction to the copper(I) state. The best preparations gave mixtures containing 93% Cu(SCN)$_2$C$_4$H$_{10}$N$_2$ with the remainder the copper(I) thiocyanate–piperazine complex. These preparations were, however, sufficiently pure to permit ready identification of the infrared absorptions due to the copper(II) thiocyanate complex.

these bands were found at 878, 890, 998, 1018, 1077, and 1122 cm^{-1}. Since this spectral region is largely dominated by skeletal and N–H deformation modes,[15] these differences probably reflect some alteration of the conformations or bond strengths in the complexes.

The positions of the thiocyanate absorptions are listed in Table II for the complexes and also for copper(I) and copper(II) thiocyanates. For ν(CS), which is most diagnostic of S or N bonding, the frequency range is 732–750 cm^{-1} for copper(I) thiocyanate and its complexes, and from 792 to 827 cm^{-1} for copper(II) thiocyanate and its complexes. The range found for the copper(I) compounds lies to slightly higher frequency than previously identified for S-bonded compounds[7] whereas the frequencies ob-

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TABLE II

POSITIONS OF THE THIOCYANATE BANDS (cm^{-1})

Compound	$\nu(CN)$ KBr	$\nu(CN)$ Nujol	$\nu(CS)$ KBr	$\nu(CS)$ Nujol	$\delta(NCS)$ KBr
CuSCN	2148	2148	732	...	412
CuSCN–pyridine	2160, 2108	2114	...	...	403
CuSCN–α-picoline	2160, 2143, 2095	2100	...	...	...
CuSCN–γ-picoline	2164, 2106	2155, 2103	750	748	447
CuSCN–3,5-lutidine	2160, 2143, 2085	2147, 2098	748	749	437
CuSCN–quinoline	2140, 2185	2143, 2103	...	...	438
$(CuSCN)_4$–(piperidine)$_3$	2158, 2145, 2093	2145, 2095	735	735 sh	440
$(CuSCN)_2$–piperazine	2158, 2112	2148, 2114	749	748	438
$(CuSCN)_4$–(pyrazine)$_3$	2150, 2085	2146, 2088	735	...	428
$(CuSCN)_6$–(2,2'-bipyridine)$_5$	2145, 2100	2150, 2108	737 sh	...	446
$Cu(SCN)_2$	2140	2138	792, 737	796, 737	468, 437
$Cu(SCN)_2$–(pyridine)$_2$	2078	2086	821	821	473, 465
$Cu(SCN)_2$–(β-picoline)$_2$	2080	2088	...	...	472
$Cu(SCN)_2$–(γ-picoline)$_2$	2070	2083	...	...	470
$Cu(SCN)_2$–piperazine	2072		797		462
$Cu(SCN)_2$–pyrazine	2106	2109	826	827	454
$Cu(SCN)_2$–(2,2'-bipyridine)$_2$	2060, 2033	2068, 2030	808	812	462

served for the copper(II) complexes clearly indicate N bonding. For those copper(I) complexes where $\nu(CS)$ could not be located in the 770–720-cm^{-1} region due to strong absorption by the organic ligands, the absence of bands between 770 and 850 cm^{-1} still argued against N bonding. Similarly, it was not possible to locate $\nu(CS)$ in the picoline complexes of copper(II) thiocyanate, but it is reasonable also to attribute N bonding in these compounds, based on the positions of $\nu(CN)$ and $\delta(NCS)$, as discussed below.

For the bending mode of the thiocyanate group, distinct frequency ranges also were found for the copper(I) and copper(II) compounds. In copper(I) thiocyanate complexes $\delta(NCS)$ was found between 403 and 447 cm^{-1} and in copper(II) thiocyanate complexes this absorption occurred between 454 and 473 cm^{-1}.

The position of the C–N stretching mode showed some correlation with the oxidation state of the metal ion although overlap of the frequency ranges was found. Thus the copper(I) thiocyanate complexes showed a very strong band between 2085 and 2114 cm^{-1} and another weaker band near 2150 cm^{-1} which in some cases was split into a doublet. The frequency range for copper(II) thiocyanate complexes was from 2060 to 2109 cm^{-1} and the bipyridine complex exhibited a doublet structure with an additional component at 2030 cm^{-1}. Uncomplexed copper(I) and copper(II) thiocyanates showed very similar, unsplit bands at 2148 and 2140 cm^{-1}, respectively.

The usual frequency attributed to bridging ligands in S-bonded thiocyanate complexes falls about 50 cm^{-1} to higher frequency relative to the position of $\nu(CN)$ for nonbridging ligands. In line with this correlation, one could postulate both bridging and terminal functionality in those S-bonded copper(I) thiocyanate complexes which exhibit two bands in the 2100-cm^{-1} region. In this case the higher energy band near 2150 cm^{-1} would be assigned to bridging thiocyanate groups and the lower frequency bands to terminal ligands. This assignment indicating bridging thiocyanate ligands would accord with the in-

soluble nature of the compounds. Furthermore, the general properties of copper(I) and copper(II) thiocyanates suggest that their crystal lattices must certainly be made up of chain structures as could be inferred from the spectral band positions which indicate only bridging thiocyanate groups.

No further correlations appear evident for the $\nu(CN)$ absorption in copper(II) thiocyanate complexes except to note that the frequency range found for this vibrational mode falls within that normally attributed to N-bonded compounds. Presumably the single case of splitting observed indicates coupling with a lattice mode.

The results reported here thus complement those of other workers who have concluded that for study of solids the position of $\nu(CS)$ is of greatest use for diagnostic purposes in deciding between S- and N-bonded thiocyanate groups but that the positions of $\nu(CN)$ and $\delta(NCS)$ also are sensitive to the mode of bonding. Of greater significance may be the demonstration that the two oxidation states of copper can be distinguished through the infrared spectra of their thiocyanate complexes. This sensitivity of the mode of bonding to oxidation state was predicted by Jørgensen[16] and could prove useful in qualitative, and possibly quantitative, analysis of copper compounds.

As Livingstone[2] has pointed out, the thiocyanate ion generally coordinates to class a metals[17] through nitrogen and to class b metals through sulfur. The copper(I) ion clearly belongs to the class b category[18] which is consistent with S bonding in its complexes. The copper(II) ion, on the other hand, has not unambiguously exhibited class a properties in its complex chemistry. However, the marked class a character of copper(II) in its thiocyanate complexes may pro-

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vide a basis for comparing the stabilities of other complexes of copper(II) with nitrogen and sulfur donors.

Experimental Section

The N-heterocyclic amines used in this investigation were commercial materials of highest available purity and were used as received.

Copper(I) thiocyanate was obtained from Alfa Inorganics. Complexes with those ligands which are liquids at 25° were prepared by dissolving the copper(I) thiocyanate in the pure liquid and precipitating the compound by dilution with ethanol. For the solid ligands, finely ground copper(I) thiocyanate was stirred at room temperature with an ethanol solution of the amine for periods of 18–36 hr. The unusual stoichiometries of the pyrazine, piperidine, and bipyridine complexes did not change when the preparations were carried out in refluxing ethanol.

The copper(II) thiocyanate complexes were obtained from the corresponding copper(II) chloride compounds by treatment with the stoichiometric quantity of potassium thiocyanate in ethanol. All of the compounds were washed with absolute ethanol and were dried under vacuum at 25°.

Infrared spectra were recorded from KBr pellets and Nujol mulls using a Beckman IR-10 spectrophotometer calibrated with polystyrene. For those compounds containing organic ligands with absorption bands near the thiocyanate bands, location of the latter was accomplished by comparison with the spectra of the corresponding copper(II) chloride–base complex. The spectrum of a copper(II) chloride complex was essentially identical with that of the free ligand.[13]

New Synthesis of a π-Crotylrhodium Complex

BY HAROLD E. SWIFT AND ROBERT J. CAPWELL, JR.

The reaction of ethanolic rhodium trichloride with olefins and dienes has been investigated quite extensively in recent years and the results have been varied. For example, a reaction between ethanol and butadiene to form ethers where rhodium trichloride acts as a catalyst has been reported.[1]

Butadiene has been polymerized to both crystalline and oily polymers in ethanol[2–4] using rhodium trichloride as a catalyst. Ethylene[5,6] and propylene[7] have been dimerized in ethanol using rhodium trichloride as a catalyst. Olefins have been isomerized with ethanolic[8] rhodium trichloride. In other cases complex formation between rhodium and olefins and/or dienes has been reported.[1,9,10]

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We now wish to report the synthesis of what is believed to be a new reaction in which a π-crotylrhodium complex is formed.

Experimental Section

The complex was formed by adding 5 g of butadiene to a flask immersed in a Dry Ice–acetone bath which contained 1.2 g of rhodium trichloride trihydrate ($RhCl_3 \cdot 3H_2O$) dissolved in 150 ml of absolute ethanol and 35 g of 10–20 mesh granular zinc metal. After the addition of butadiene, the flask was removed from the Dry Ice–acetone bath and set aside to warm slowly at room temperature. Approximately 30 min after the flask was removed from the bath, a light brown precipitate started to form around the zinc granules. After the reaction ceased, the precipitate was filtered and washed several times with absolute ethanol. Separation of the precipitate from the zinc granules presented no problem since the precipitate could be easily suspended in ethanol, whereas the zinc granules remained at the bottom of the flask. After thoroughly washing the precipitate with absolute ethanol, it was dried under vacuum at 70°. The solid obtained weighed 0.45 g. No precautions were taken to carry out the reaction and separation in an inert atmosphere.

Zinc concentrations in solutions were determined by X-ray emission spectroscopy (X-ray fluorescence). Zinc metal was dissolved in dilute HCl for the primary standards. Aliquots were diluted with ethanol for use as working standards. Copper was added to the standards and the samples as an internal standard to correct for absorption effects by rhodium. The Zn Kα/Cu Kα intensity ratios were then determined for standards and samples.

Infrared spectra were recorded in the 4000–550-cm^{-1} region with a Perkin-Elmer Model 421 spectrophotometer. The vibrational frequencies were measured both with a KBr wafer and in Nujol mull. In the 550–200-cm^{-1} region, a Perkin-Elmer Model 621 was used and the spectra were obtained in Nujol between polyethylene windows.

Results and Discussion

The reaction described above was an attempt to form a rhodium(I) butadiene complex using a similar type of reaction where copper has been used to prepare a rhodium(I) carbonyl complex[11]

$$RhX_3 + 2CO + 2Cu \longrightarrow Rh(CO)_2X + Cu_2X_2 \qquad (1)$$
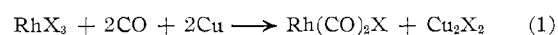
The complex reported in this paper contained 19.1% carbon, 3.6% hydrogen, 24.1% chlorine and 40.1% rhodium. The only analysis which was questionable was the rhodium where there was a ±2% spread among three samples from the same batch.

An infrared spectrum of the solid showed strong water bands at 3300 and 1607 cm^{-1}. This water was tenaciously held since it could not be removed under vacuum at 100°. Also, between 4000 and 500 cm^{-1}, absorptions were found at 1456 (m), 1434 (s), 1370 (ms), 1245 (w), 1181 (w), 1023 (s), 964 (ms), 868 (m), and 535 (m, br) cm^{-1}. Fritz[12] and Fischer and Werner[13] have reported these bands as characteristic of the π-crotyl system. However, the 1434-cm^{-1} band has remained unassigned, and, therefore, we suggest it is a methyl deformation. Between 500 and 200 cm^{-1}, a very strong band at 330 cm^{-1} and a medium intense one at 280 cm^{-1} were observed. Following the assignments made by Powell and Shaw[9] for

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