affirms a tighter metal–amino bond in the former complex.

The extremely weak band at 385 cm^{-1} is attributed to a metal–oxygen stretching mode. The metal–oxygen stretch in the mercury(II)–aquo complex has been detected at 380 cm^{-1}.[7] The possible assignment of this band to the glycine complex would be consistent with infrared studies on other metal–glycine systems.[5] As no other line attributable to a metal–oxygen frequency is observed, it is impossible to distinguish whether this band is due to a mercury–aquo or mercury–glycino complex or both. The formation of a bidentate complex with binding by the carboxylate group is indicated by the appearance of a strong line due to a carbon–carbon stretch in the chelate at 912 cm^{-1} and by the appearance of a chelate ring deformation mode at 230 cm^{-1}. Condrate and Nakamoto's analysis[5] indicates that such a ring mode should be observed at *ca.* 215 cm^{-1}, but this vibration remained undetected in their measurements which were extended to only 250 cm^{-1}. The line at 298 cm^{-1} is assigned to the CCN bending of the free glycine in agreement with the calculated frequency range of 297–308 cm^{-1}.[4] This bending frequency would be expected to increase in energy upon chelation, and the line at 325 cm^{-1} may be ascribed to the analogous vibration in the metal complex. Unfortunately, with the exception of the 464-cm^{-1} line, the weak intensities of the low-frequency bands precluded polarization studies.

Whereas chelation may be confirmed by the appearance of new bands at low energies, complementary evidence from frequency shifts is obtained in the high-frequency region. Although some glycine remains in the free cationic form at pH 1.5, deprotonation and binding of the carboxylate group to the Hg(II) is indicated by the shift in the C–C stretch from 869 to 912 cm^{-1}. The shifts observed in the CO_2^- antisymmetric stretching frequency are of particular interest. This mode appears in the Raman spectra at 1611, 1615, and 1644 cm^{-1} in the anionic, zwitterionic, and cationic forms of free glycine.[8] The shift upon protonation of the amino group has been attributed to an inductive effect accompanying increase in positive charge on the nitrogen atom.[9] For the amino acids cysteine[10] and alanine[11] it has been argued that the increase in this frequency upon complexation to a variety of metals can be used as a measure of the relative enthalpies of formation of the metal–nitrogen bond. This empirical correlation depends on a small shift in the antisymmetric carboxylate frequency upon complexation of the carboxylate group and a substantial frequency shift of this mode upon protonation of the nitrogen of the anion to form the zwitterion.[10,11] For glycine there is a relatively large increase in the antisymmetric carboxylate frequency on protonation of the carboxylate group ($\Delta\nu = 29$ cm^{-1}), while the shift in this frequency upon forming the zwitterion is only 4 cm^{-1}.[8] Since it is apparent that neither of the conditions on which the enthalpy–carboxylate frequency correlation was based in the alanine and cysteine systems holds for the glycine case, it is not surprising that one observes a decrease in the frequency of the antisymmetric carboxylate stretch in the zinc–, cadmium–, and mercury–glycine complexes (recorded at 1610, 1600, and 1589 cm^{-1}, respectively). An examination of the potential energy distributions for glycine[4] and its complexes[5] reveals that other vibrations contribute significantly to the observed frequency at *ca.* 1600 cm^{-1}, and this may not be ignored in eliciting secondary information from frequency shifts upon glycine coordination.

For the glycine complexes an alternate criterion for the strength of a chelate bond is the frequency attributable principally to the metal–ligand vibration. Although other normal modes do affect this frequency, the main contributions arise from low-frequency motions that appear only on complex formation or modes directly involving the ligand atom participating in the complex bond of interest. For the glycine complexes this criterion would support the ordering of metal–nitrogen bond strengths for divalent metals: Pt(II) (554, 549 cm^{-1}) $\sim$ Pd(II) (550 cm^{-1}) $>$ Hg(II) (464 cm^{-1}) $\sim$ Cu(II) (460, 439 cm^{-1}) $>$ Ni(II) (439 cm^{-1}) $>$ Zn(II) (430 cm^{-1}) $>$ Cd(II) (415 cm^{-1}), in complete agreement with the stability of these complexes.[12]

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[8] S. A. S. Ghazanfar, D. V. Myers, and J. T. Edsall, *J. Am. Chem. Soc.*, **86**, 3439 (1964).

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Infrared Spectra in Polarized Light of $Na_2[Fe(NO)(CN)_5]\cdot 2H_2O$

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The assignment of the M–N stretching and M–NO rocking frequencies of nitrosyl complexes has been made so far only for the compound [Co(NO)(CO)$_3$].[1] By isotopic substitution with ^{15}N it has been possible to assign the absorption bands at 594 and 565 cm^{-1} to the Co–N stretching and Co–NO rocking frequencies, respectively.

The infrared spectrum of nitrosyl complexes of the type $[M(NO)(CN)_5]^{n-}$ usually exhibits two absorption bands in the 670–600-cm^{-1} region, while the complexes of the type $[M(NO)X_5]^{n-}$ exhibit two bands in the 620–530-cm^{-1} region.[2,3] The assignment of these absorption bands is till controversial. Some authors

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[1] R. S. McDowell, W. D. Horrocks, and J. Yates, *J. Chem. Phys.*, **34**, 530 (1961).

[2] M. B. Fairey and R. J. Irving, *Spectrochim. Acta*, **22**, 359 (1966).

[3] P. Gans, A. Sabatini, and L. Sacconi, *Inorg. Chem.*, **5**, 1877 (1966).

assign them to M–NO rocking and M–N stretching vibrations,[3] while other authors attribute them only to M–N stretching vibrations, leaving the M–NO rocking vibration unassigned.[2]

The question may be solved with the aid of new experimental data, such as Raman and infrared spectra of isotopic molecules, measurements of line polarization of Raman spectra, or infrared spectra on single crystals using polarized light. This note reports the results obtained from the measurement of the infrared spectra of single crystals of $Na_2[Fe(NO)(CN)_5] \cdot 2H_2O$ using polarized light.

Experimental Section

Single crystals of $Na_2[Fe(NO)(CN)_5] \cdot 2H_2O$ were grown according to the procedure described in ref 4. Crystals 20 mm long and approximately 6 mm wide were obtained. The crystals are best described as rhombic prisms elongated along the *a* axis. The most developed faces belong to the forms {011}, {001}, and {101}.

A plane surface perpendicular to the desired axis was obtained by grinding the crystal with very fine sandpaper. The plane surface was then polished in the following manner. Some Al_2O_3 powder was put on a chamois cloth and wet with a few drops of alcohol; the plane surface was rubbed on this cloth until a fine, smooth surface was obtained. This plane surface was next glued to a metal disk with a hole in the center of 2-mm diameter. The opposite side of the crystal was then ground with sandpaper to obtain a thin section and then was polished as before.

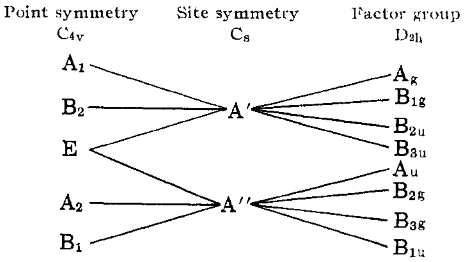
The metal disk was placed in a normal cell for solids and the spectra were measured with a Perkin-Elmer Model 225 spectrophotometer using a polarizer of AgCl plates.

The thinnest sections of $Na_2[Fe(NO)(CN)_5] \cdot 2H_2O$ which were obtained had a thickness of about 0.03 mm. However in the O—H stretching region and below 600 cm^{-1} almost total absorption of radiation occurred. On the contrary, it was possible to measure the spectra in the C≡N and M—N stretching regions because the strongest bands in these regions absorbed about 95% of the radiation. Numerous attempts to obtain thinner sections were unsuccessful owing to the fragility of the thin sections of the crystal.

Discussion

The compound $Na_2[Fe(NO)(CN)_5] \cdot 2H_2O$ crystallizes in the space group D_{2h}^{12}-Pnnm with four molecules per unit cell.[5] The site symmetry of the nitroprusside ion is C_s with the Fe–NO axis lying in the plane of symmetry. The *c* axis of the crystal is perpendicular to the plane of symmetry. The $[Fe(NO)(CN)_5]^{2-}$ ion in the crystal has approximately C_{4v} symmetry, which is the symmetry expected for the free ion. From Chart I it can be seen that the M–N stretching vibration of species A_1 in the free ion becomes that of species A′ in the site symmetry C_s and gives rise to infrared absorptions polarized along the *a* and *b* axes of the crystal. The M–NO rocking vibration of species E in the free ion is split into the species A′ and A″ in the site symmetry C_s and gives rise to infrared absorptions polarized along the three axes of the crystal.

CHART I[a]



[a] The *z* axis in the point group D_{2h} is perpendicular to the plane of symmetry of the point group C_s. T_z belongs to the species B_{1u} in the point group D_{2h}.

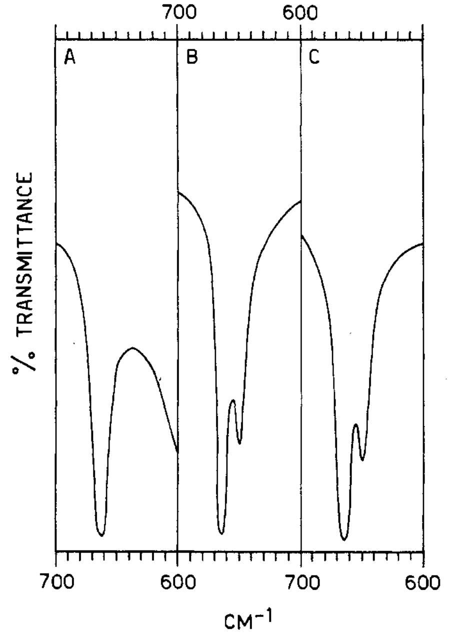


Figure 1.—Infrared spectra in polarized light in the 700–600-cm^{-1} region: A, section perpendicular to the *a* axis, polarization parallel to the *c* axis; B, section perpendicular to the *a* axis, polarization parallel to the *b* axis; C, section perpendicular to the *b* axis, polarization parallel to the *a* axis.

The spectra (Figure 1) show that the absorption band at 650 cm^{-1} is absent when the plane of the polarized light is parallel to the *c* axis while the band at 662 cm^{-1} appear in all cases. The first frequency can thus be assigned to the M–N stretching vibration and the second to the M–NO rocking vibration. Thus the infrared spectra using polarized light support the assignment of these two absorption bands to M–N stretching and M–NO rocking vibrations.

The Fe(II)–N stretching frequency is the highest until now observed for vibrations of this type. This vibration has, for example, a frequency of 306 cm^{-1} for the compound $[Fe(NH_3)_6]I_2$.[6] In the amine complex, however, the nitrogen atom can only form a single σ bond with the metal atom while the nitrosyl group forms also π bonds. A detailed MO calculation of $[Fe(NO)(CN)_5]^{2-}$ ion performed by Manoharan and Gray[7] shows in fact that there is substantial Fe→NO back-bonding. Thus the NO group is strongly bound to the iron atom and this is further shown by the exceptionally short Fe–N distance of 1.63 A.[5] The high value for the Fe–N stretching frequency therefore appears reasonable.

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(4) J. J. Gilman, "The Art and Science of Growing Crystals," John Wiley and Sons, Inc., New York, N. Y., 1963, p 203.

(5) P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, **2**, 1043 (1963).

(6) L. Sacconi, Al Sabatini, and P. Gans, *ibid.*, **3**, 1772 (1964).

(7) P. T. Manoharan and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 3340 (1965).

The spectrum in the C≡N stretching region constitutes a good example of how measurements with polarized light permit the assignment of the various vibrations to the symmetry species to which they belong.

In the free ion the C≡N stretching vibrations divide among the symmetry species as follows: $2A_1 + E + B_1$. From Chart I it can be seen that the vibrations of species A_1 are polarized along the *a* and *b* axes, the vibrations of species E are polarized along the three axes, and the vibrations of species B_1 are polarized only along the *c* axis. The spectrum in Figure 2 indicates that the absorption bands observed at 2175 and 2163 cm^{-1} correspond to vibrations of species A_1, the band at 2145 cm^{-1} corresponds to the vibration of species E, and the band at 2158 cm^{-1} corresponds to the vibration of species B_1.

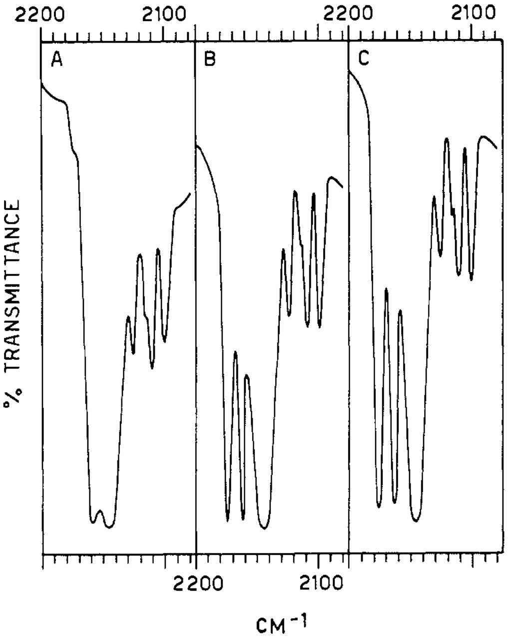

Figure 2.—Infrared spectra in polarized light in the 2200–2100-cm^{-1} region: A, section perpendicular to the *a* axis, polarization parallel to the *c* axis; B, section perpendicular to the *a* axis, polarization parallel to the *b* axis; C, section perpendicular to the *b* axis, polarization parallel to the *a* axis.

The weaker absorption bands observed between 2130 and 2100 cm^{-1} may be attributed to combinations of C≡N fundamentals with lattice vibrations situated at about 45 cm^{-1} or to C≡N stretchings of cyano groups with ^{13}C. The spectrum of $Na_2[Fe(NO)(CN)_5] \cdot 2H_2O$ in KBr pellets at liquid nitrogen temperature shows a slight increase in intensity and in frequency (about 4 cm^{-1}) both of these bands and of the C≡N fundamentals with respect to the spectrum measured at room temperature. If these bands are combinations of lattice modes with the C≡N fundamentals, they must be difference bands and if so then there are three consequences: (1) sum bands should also be observed; (2) lowering the temperature should reduce the intensity of the difference bands;[8] (3) since the frequency of lattice vibrations increases markedly by lowering the temperature, the frequency of the difference bands should decrease. Since none of these three effects is observed, this explanation seems to be ruled out. Thus it appears reasonable to attribute these bands to C≡N stretchings of cyano groups with ^{13}C.

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Infrared Detection of Xenon Dichloride

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Thus far, definitive evidence concerning inert gas–halogen compounds has been restricted to fluorides. Rundle and co-workers made encouraging observations that suggested the existence of xenon chlorides.[1] Persistent efforts to exploit this report in the Berkeley laboratories failed to give positive results.[2] Only very recently has real progress been reported when Meinert[3] offered mass spectrometric evidence that he had isolated a compound containing xenon and chlorine, possibly xenon dichloride. Using techniques resembling those of Meinert, we have at last obtained the infrared spectrum of xenon dichloride.

Mixtures of xenon and chlorine (Xe/Cl_2 = 200–100) were passed through a microwave discharge (2450 mc, RK 5609, Raytheon Corp.) and then condensed upon a cesium iodide optical window maintained at 20°K. Infrared spectra were then recorded from 4000 to 200 cm^{-1} on a Perkin-Elmer 225 grating infrared spectrophotometer (frequency accuracy, ± 0.2 cm^{-1}; spectral slit width, 0.4 cm^{-1}). A broad, structured absorption centered near 313 cm^{-1} was observed which was not observed when chlorine alone passed through the glow discharge. The band was reproduced, however, if xenon was deposited through a separate jet convergent at the cold window with the excited chlorine stream. Figure 1 shows this absorption under optimum resolution.

If the 313-cm^{-1} feature is due to a xenon chloride, then a complex structure can be expected because of the isotopic complexity (xenon has seven isotopes above 1% natural abundance). The hypothesis that the spectrum is due to xenon dichloride can be reasonably tested by attempting to reproduce this spectrum through calculations. Two parameters are needed, a force constant and a characteristic line shape. To fix the force

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(8) The author is indebted to a referee for these two suggestions.

(1) R. E. Rundle to G. C. Pimentel, private communication, 1963.

(2) See R. D. Spratley, Ph.D. Thesis, University of California, Berkeley, Calif., 1965.

(3) H. Meinert, *Z. Chem.*, **6**, 71 (1966).