the dissociative path is probably very rapid even in alkaline solution at 0° and, further, that a bimolecular path is expected to be important because of the possibility of forming a transition state by attachment of an ethylenediamine molecule in an axial position. Thus, bimolecular exchange may occur through rapid formation and dissociation of the tris complex, in spite of its low thermodynamic stability constant.[13] Bjerrum and Nielsen suggested that the third ethylenediamine molecule in the tris complex is monodentate and that copper(II) has coördination number 5 in the complex. Although such a structure may be involved as an initial step in the reaction, it cannot be the only form of the tris complex. If proton exchange results reported in this paper are indeed explained by the bimolecular exchange of ethylenediamine, it is necessary that the ethylenediamine ligands be equivalent in some intermediate or transition state, most probably one having nearly octahedral symmetry. It should be noted that the bimolecular exchange rate constant expressed in terms of ethylenediamine exchange is

$$k_{en}' = k_H'/4 \qquad (13)$$

because there are four exchangeable protons in each ethylenediamine molecule.

The observed activation energy, 4.5 kcal./mole, is abnormally low for unimolecular (or pseudo-unimolecular) dissociation of a transition metal–ethylenediamine chelate. However, it is quite reasonable for an "associative" reaction

$$Cu(en)_2(H_2O)_2^{++} + en \longrightarrow Cu(en)_3^{++} + 2H_2O \qquad (14)$$

If that reaction involves the rate-determining step in proton exchange, the ensuing "dissociation"

$$Cu(en)_3^{++} + 2H_2O \longrightarrow Cu(en)_2(H_2O)_2^{++} + en \qquad (15)$$

must be rapid, in spite of an anticipated high activation energy, because of a large entropy of activation.

AUSTIN, TEXAS

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(13) J. Bjerrum and E. J. Nielsen, *Acta Chem. Scand.*, **2**, 297 (1948).

[CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORY, UNIVERSITY OF ILLINOIS]

The Infrared Spectra of Some Thiocyanatocobalt Ammines

BY MARK M. CHAMBERLAIN[1] AND JOHN C. BAILAR, JR.

RECEIVED NOVEMBER 22, 1958

The infrared spectra of a series of thiocyanatocobalt ammines has been obtained in the region from 680 to 4000 cm.$^{-1}$. The spectra strongly suggest the formation of a double bond between the ligand and the metal with resulting loss of triple bond character in the C–N bond and gain of double bond character in the C–S bond. It has been shown that coördinated and ionic thiocyanate can be differentiated readily by examination of their infrared spectra. Bridging by thiocyanate occurs in some of the thiocyanatocobalt ammine–silver addition compounds and can be detected by observing the C–N frequency of the adduct. Assignment of bands in the infrared spectra of some acido bisethylenediamine complexes to various N–H vibrations has been made and a means for differentiating *cis*- and *trans*-isomers of these compounds by the number of bands in the 1120–1150 cm.$^{-1}$ region proposed.

The introduction of the thiocyanato group into the coördination sphere of various cobalt ammines gives rise to a series of compounds which differ markedly in chemical and physical properties from the usual halo-substituted acido cobalt ammines. For example, the thiocyanato ligand of the thiocyanatocobalt ammines is more resistant to replacement by the anions of strong mineral acids or by water[2] than are the comparable chloro- or bromocobalt ammines which undergo replacement reactions readily.[3]

Further, the thiocyanato ligand is difunctional, with both the nitrogen and the sulfur atoms potentially able to act as electron pair donors. Thiocyanate coördinates to cobalt with the formation of metal–NCS bonds and to mercury or platinum with the formation of metal–SCN bonds. Even after coördination through the nitrogen end of the molecule, the sulfur end appears to remain able to donate electrons in coördinate covalent bond formation with such metal ions as mercury(II) or silver (I). Werner[4] believed that in the thiocyanatocobalt ammines, the bonding of the ligand to the metal is through nitrogen and has claimed that the formation of the silver addition products of these ammines is due to the coördination of the heavy metal ion to the free sulfur end of the ligand. Waggener, *et al.*,[5] have demonstrated the existence of a metal to nitrogen bond in the thiocyanatocobalt ammines and their chromium analogs and have shown both that the silver adducts are much less stable than Werner had supposed and that mercury(II) ion also forms adducts with thiocyanato complexes.

In this study, the infrared spectra of a series of thiocyanatocobalt ammines and related thiocyanato complexes were obtained in an effort to determine the nature of the bonding within the thiocyanato ligand and by inference, the bonding between the ligand and the metal. Further, the difference between coördinated and uncoördinated thiocyanate and the nature of the silver adducts of some thiocyanatocobalt ammines were investigated. Finally, information leading to the assignment of various N–H vibrations in the spectra of the ethylenediamine cobalt complexes was obtained.

Experimental

Preparation of Compounds.—The preparation of pure salts of the thiocyanatocobalt ammines followed the methods of Werner and Muller.[6]

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(1) This material was taken from the Ph.D. dissertation of Mark M. Chamberlain, University of Illinois, June, 1956.

(2) J. Sand and G. Bokman, *Ber.*, **40**, 4497 (1907).

(3) A. Werner, *Z. anorg. allgem. Chem.*, **22**, 91 (1900).

(4) A. Werner, *Ann.*, **386**, 1 (1912).

(5) W. C. Waggener, J. A. Mattern and G. H. Cartledge, Abstracts of papers, 122nd National Meeting, American Chemical Society, September, 1952, page 19-P; W. C. Waggener, private communication.

(6) A. Werner and H. Muller, *Z. anorg. allgem. Chem.*, **22**, 91 (1900).

Partially deuterated *cis*- and *trans*-bisthiocyanato-bisethylenediaminecobalt(III) thiocyanate were prepared by boiling 500 mg. of the complex with one milliliter of 99.5% deuterium oxide and removing unreacted deuterium oxide and water under high vacuum.

Potassium hexathiocyanatoplatinate(IV) was prepared by the method of Bruckton[7] by the reaction of stoichiometric quantities of potassium hexachloroplatinate(IV) and potassium thiocyanate.

The compounds $MHg(SCN)_4$, in which M is cobalt(II), cadmium(II), zinc(II) iron(II), copper(II) and nickel(II), were prepared by the method of Rosenheim and Cohn.[8]

Preparation of the Silver Addition Products of the Thiocyanatocobalt Ammines. $[Co(NH_3)_5NCS](NO_3)_2 \cdot AgNO_3$.—On addition of a large excess of silver nitrate to a warm solution of 0.326 g. (0.001 mole) of thiocyanatopentamminecobalt(III) nitrate in 250 ml. of water, the orange-red solution changed to a light yellow. After standing at room temperature 45 minutes, the yellow solution yielded a golden brown precipitate. This was removed by filtration, washed with ice-water, alcohol and ether and dried over concentrated sulfuric acid.

Anal. Calcd. for $[Co(NH_3)_5NCS](NO_3)_2 \cdot AgNO_3$: C, 2.42; H, 3.02; N, 25.40; Ag, 21.70. Found: C, 2.84; H, 4.79; N, 24.25; Ag, 26.60. Ratio C:H:N:Ag found 1:20.0:7.27:1.04.

$[Co(NH_3)_5NCS](ClO_4)_2 \cdot AgClO_4$.—One millimole (0.401 g.) of thiocyanatopentamminecobalt(III) perchlorate was dissolved in 250 ml. of warm water to give an orange-red solution. No change in color was observed when one millimole of silver perchlorate in 2 ml. of water was added. When a large excess of silver perchlorate was added, a precipitate formed immediately. This was removed by filtration, washed with alcohol and ether, and dried over phosphorus(V) oxide.

Anal. Calcd. for $[Co(NH_3)_5NCS](ClO_4)_2 \cdot AgClO_4$: N, 13.81. Found: N, 15.10.

trans-$[Coen_2(NCS)_2]ClO_4 \cdot AgClO_4$.—A warm solution of 0.275 g. (0.001 mole) of *trans*-bis-thiocyanato-bisethylenediaminecobalt(III) perchlorate in 200 ml. of water was poured into a solution of 0.002 mole of silver perchlorate in 50 ml. of water. Three milliliters of 1 *N* perchloric acid was added and the heavy, slowly forming precipitate was removed by filtration, washed and dried over phosphorus(V) oxide.

Anal. Calcd. for $[Coen_2(NCS)_2]ClO_4 \cdot AgClO_4$: C, 11.96; H, 2.58; N, 13.96. Found: C, 11.71; H, 2.87; N, 13.60.

cis-$[Coen_2(NCS)_2]ClO_4 \cdot AgClO_4$.—Two millimoles (0.416 g.) of silver perchlorate in 5 ml. of water was added with stirring to a solution of one millimole (0.275 g.) of *cis*-bis-thiocyanato-bisethylenediaminecobalt(III) perchlorate in 500 ml. of water. The orange precipitate which formed immediately was removed by filtration. washed with two 5-ml. portions of ice-water, then with alcohol and ether and dried over phosphorus(V) oxide.

Anal. Calcd. for *cis*-$[Coen_2(NCS)_2]ClO_4 \cdot AgClO_4$: C, 11.96; H, 2.58; N, 13.96. Found: C, 11.84; H, 2.68; N, 13.75, 14.04.

Apparatus. Infrared Analysis.—The instruments used were: (1) a double-beam Perkin–Elmer Model 21 recording infrared spectrograph using a sodium chloride prism and calibrated against gaseous ammonia; (2) a single beam Perkin–Elmer Model 12-C recording infrared spectrograph using a lithium fluoride prism and calibrated against gaseous hydrogen chloride, water vapor and carbon dioxide. Part of the carbon dioxide spectrum was recorded on each graph from the single-beam instrument as a check point.

The "mineral-oil mull" technique was employed in preparing all solid samples for analysis. The "potassium bromide disk" method was considered but rejected since it has been found that, under the conditions employed in preparing the alkali halide disks, both cyano and thiocyanato complexes undergo reactions with the halide which may lead to ambiguous results.[9,10]

Potentiometric studies of the systems silver perchlorate–thiocyanatocobalt ammine were made using a Rubicon High Precision Type B potentiometer, serial number 89213, accurate to ±0.0001 volt in connection with a Rubicon mirror type galvanometer, serial number 88541, with a sensitivity of 1.5 mv./mm. The titration cell

$$Ag/\text{complex, } 0.1\ M\ NaClO_4//\text{satd. } NaNO_3//\text{satd. } KCl/Hg\text{–}HgCl_2$$

was constructed and immersed in a thermostated temperature bath kept at 25.0 ± 0.1°. Increments of silver perchlorate (0.4644 ± 0.0002 *M*) were added from a buret which could be read to ±0.001 ml.

TABLE I

ABSORPTION FREQUENCIES OF SOME HEAVY METAL THIOCYANATE COMPLEXES[a]

Compound	A, cm.$^{-1}$	s,sp B, cm.$^{-1}$	w,sp C, cm.$^{-1}$	w,sp D, cm.$^{-1}$ m,sp
KNCS	2066	970	954	748
$K_2Hg(SCN)_4$	2100	923	900	716
$CoHg(SCN)_4$	2142	940	895	793
$ZnHg(SCN)_4$	2150	942	895	786
$CdHg(SCN)_4$	2130	932	887	775
$FeHg(SCN)_4$	2129	938	897	788
$NiHg(SCN)_4$	2155	922	863	737
$CuHg(SCN)_4$	2140	927	872	799, 764
$K_2Pt(SCN)_6$	2125, 2115	920	847	694

[a] s = strong, m = medium, w = weak, sp = sharp; assignments[11]: A, C–N stretch; B, bending overtone; C, bending combination; D, C–S stretch.

TABLE II

THIOCYANATE C–N AND C–S STRETCHING FREQUENCIES[a]

Compound	C–N, cm.$^{-1}$	C–S, cm.$^{-1}$
$[Co(NH_3)_5NCS]Cl_2$	2141s,sp	810
$[Co(NH_3)_5NCS](NO_3)_2$	2120s,sp	809
$[Co(NH_3)_5NCS](NO_3)_2 \cdot AgNO_3$	2112s,sp	810
trans-$[Co(NH_3)_4(NCS)_2]Cl$	2112s,b	803
$[Co\ en_3](NCS)_3$	2065, 2035 split	757
trans-$[Co\ en_2Cl_2]NCS$	2066s,sp	755
trans-$[Co\ en_2Cl(NCS)]Br$	2117s,sp	790
trans-$[Co\ en_2Cl(NCS)]NCS$	2140sh, 2060s,sp	787, 732
cis-$[Co\ en_2Cl(NCS)]NCS \cdot H_2O$	2134s,sp, 2102sh	810, 775
cis-$[Co\ en_2Cl(NCS)]ClO_4$	2135s,sp	....[b]
trans-$[Co\ en_2(NCS)_2]Cl \cdot H_2O$	2136s,b	787
trans-$[Co\ en_2(NCS)_2]NCS$	2080s,vb	793, 755
cis-$[Co\ en_2(NCS)_2]Cl \cdot H_2O$	2122sh, 2110s,sp	812
cis-$[Co\ en_2(NCS)_2]NCS$	2137sh, 2117s,sp 2100sh	807, 747
cis-$[Co\ en_2(NCS)_2]ClO_4$	2125s,sp	....[b]
cis-$[Co\ en_2(NCS)_2]ClO_4 \cdot AgClO_4$	2152s,sp	....[b]

[a] s = strong, sp = sharp, sh = shoulder, b = broad, v = very. [b] C–S frequency obscured by the strong, broad ClO_4^- absorption.

TABLE III

cis- *vs.* *trans*-BISETHYLENEDIAMINECOBALT(III) COMPLEXES 1100–1150 cm.$^{-1}$ region

Compound	*cis*-isomer	*trans*-isomer
$[Co\ en_2Cl_2]Cl$	1137s,sp—1121s,sp	1127s,sp
$[Co\ en_2Cl(NCS)]NCS$	1142m,sp— ....[a]	1127s,sp
$[Co\ en_2(NCS)_2]Cl$	1134s,sp—1116s,sp	1124s,sp
$[Co\ en_2(NCS)_2]NCS$	1144s,sp—1124s,sp	1125s,sp

[a] Spectra not clearly resolved.

Discussion of Results

The Structure of Coördinated Thiocyanate.—In the rock-salt region of the infrared spectrum

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[7] G. B. Bruckton, *J. Chem.*, **7**, 22 (1854).

[8] A. Rosenheim and R. Cohn, *Z. anorg. Chem.*, **27**, 280 (1904).

[9] L. H. Jones and M. M. Chamberlain, *J. Chem. Phys.*, **25**, 365 (1956).

[10] L. H. Jones and M. M. Chamberlain, unpublished results.

[11] L. H. Jones, *J. Chem. Phys.*, **25**, 1069 (1956).

TABLE IV

DEUTERATED *cis*- AND *trans*-[Co $en_2(NCS)_2$]NCS

N–H *vs.* N–D absorption frequencies, $cm.^{-1}$

cis-isomer		*trans*-isomer	
N–H	N–D	N–H	N–D
3250	2380	3220	2380
3160	2350	3150	2350
3065	2280	3060	2285
1600	1192	1594	1193
1585	1176	1575	1180
1568	1155	..	..
1144	937	1126	939
1123	927	..	..

(4000 to 600 $cm.^{-1}$) two fundamental vibrations associated with coördinated thiocyanate appear: the carbon-nitrogen stretching vibration (A) and the carbon–sulfur stretching vibration (B).

$$\text{(A)}\quad \text{Co–}\overset{\leftarrow}{\text{N}}\text{–}\overset{\rightarrow}{\text{C}}\text{–S}$$

$$\text{(B)}\quad \text{Co–N–}\overset{\leftarrow}{\text{C}}\text{–}\overset{\rightarrow}{\text{S}}$$

In thiocyanatopentamminecobalt(III) chloride, absorption bands are observed at 2141 and 803 $cm.^{-1}$ for the carbon–nitrogen and the carbon-sulfur stretching vibrations, respectively; in *trans*-[Co $en_2Cl(NCS)$]Br these absorption bands appear at 2117 and 790 $cm.^{-1}$; in *cis*-[Co $en_2Cl(NCS)$]-NCS at 2134 and 810 $cm.^{-1}$.

One possible electronic structure for coördinated thiocyanate may be represented as: Co—N≡C—S implying a carbon–nitrogen triple bond and a carbon–sulfur single bond. Were this picture an exact description of the bonding within coördinated thiocyanate, the absorption for the carbon–nitrogen stretching vibration should appear at about 2250 $cm.^{-1}$ as in the organic nitriles[12] and the absorption for the carbon–sulfur stretching vibration in the frequency range 600–700 $cm.^{-1}$.[13,14]

Comparison of the observed infrared absorption frequencies of coördinated thiocyanate with these reference values indicates (1) that the C–N stretching frequency has been shifted toward lower wave numbers, implying some loss of triple bond character in the C–N bond, and (2) the C–S stretching frequency is shifted toward higher wave numbers, implying a gain of double bond character in this link.

At least two explanations can be presented to explain this change in bond character within coördinated thiocyanate.

(1) The shift of the C–N frequency toward the value of 2066 $cm.^{-1}$ and the increase of the C–S frequency may be attributed to an increase in ionic character of the metal to thiocyanate bond.

(2) For nickel carbonyl, Pauling[15] proposes resonance structures involving a nickel to carbon double bond. The resonance hybrid is pictured as containing partial double bonds between carbon and nickel and between carbon and oxygen. Similar resonance forms may be written for the ferrocyanide ion.

In terms of the molecular orbital approach, the sigma portion of the metal to ligand double bond would be formed by direct donation of an unshared pair of electrons by the ligand to the metal; the pi portion of the bond by donation of an electron pair from a filled "d" orbital of the metal. The formation of such a double bond between metal and ligand often requires that the electrons within the ligand rearrange themselves and, usually, this rearrangement is pictured so that at most only eight electrons are associated with each atom.

In the case of nickel carbonyl, the formation of a metal to ligand double bond and subsequent rearrangement of electrons within the ligand leads to a loss of triple bond character in the carbon to oxygen bond. If similar reasoning is applied to double bond formation between cobalt and thiocyanate, rearrangement of the electrons in the ligand leads to loss of triple bond character in the nitrogen to carbon bond, a gain in double bond character in the carbon to sulfur bond, and an expansion of the octet about sulfur to accommodate ten electrons.

Additional support for this second proposed explanation is found in the fact that thiocyanate is a good *trans* director and, according to Chatt, *et al.*,[16] such a ligand should exhibit definite tendencies toward double bond formation with the central metal.

Until the absorption frequency of the cobalt–thiocyanate bond is determined and compared with a frequency which can be attributed solely to a cobalt to nitrogen single bond, the exact nature of the cobalt to thiocyanate bond must remain in doubt.

In *cis*- and *trans*-[Co $en_2(NCS)_2$]X, an entirely different set of vibrations must be considered. In the *trans*-isomer, there are two sets of vibrations associated with the C–N group, an asymmetric vibration which is infrared active and a symmetric vibration which is infrared inactive. The spectra of *trans*-[Co $en_2(NCS)_2$]Cl and *trans*-[$Co(NH_3)_4$-$(NCS)_2$]Cl do indeed differ from the spectrum of [$Co(NH_3)_5NCS$]Cl_2 in that the band in the 2100 $cm.^{-1}$ region is broadened considerably and shifted to slightly lower frequencies.

In the *cis*-isomer there is again one infrared active asymmetric vibration but the symmetric vibration is now also infrared active. In the spectrum of *cis*-[Co $en_2(NCS)_2$]Cl a strong band is observed in the 2100 $cm.^{-1}$ region but a well-defined shoulder also appears which may be associated with the infrared active symmetric vibration.

It should be noted that in all cases in which thiocyanate is present both as the ion and as a coördinated group, the two species can be differentiated on the basis of their infrared spectra. The ionic thiocyanate absorbs below 2100 $cm.^{-1}$ and at 750 $cm.^{-1}$. The C–S stretching vibration absorption at 750 $cm.^{-1}$ is better for this differentiation than the C–N absorption since the latter is sometimes obscured by the broad absorption in the *trans*-bisthiocyanato complexes.

In those compounds in which thiocyanate is coördinated to a heavy metal through sulfur,

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[12] M. F. Amr El-Sayed and R. K. Sheline, *J. Inorg. and Nucl. Chem.*, **6**, 187 (1958).

[13] S. Mizushima, *et al.*, *J. Phys. Chem.*, **59**, 293 (1955).

[14] C. I. Beard and B. P. Dailey, THIS JOURNAL, **71**, 929 (1949).

[15] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., p. 251.

[16] J. Chatt, L. A. Duncanson and L. M. Venanzi, *J. Chem. Soc.*, 4456 (1955).

e.g., $K_2Hg(SCN)_4$ and $K_2Pt(SCN)_6$,[17] broadening of the absorption band associated with the carbon–nitrogen stretching vibration makes exact location of the frequency difficult. The carbon–sulfur frequencies, however, remain sharp and are lowered to 716 and 694 cm.$^{-1}$, respectively, as compared to the values 780 to 810 cm.$^{-1}$ observed for those compounds with a metal to nitrogen bond.

Jeffery[18] reports X-ray evidence indicating a mercury to sulfur single bond in the compound $CoHg(SCN)_4$ and states that the cobalt is so located as to be within bonding distance of the nitrogen. The infrared spectrum of this compound shows a carbon–nitrogen stretching frequency at 2137 cm.$^{-1}$ and a carbon–sulfur stretching frequency at 793 cm.$^{-1}$. In the analogous compounds in which cobalt(II) is replaced by other divalent metals, these vibrations occur at approximately the same frequencies. The large difference between the carbon–sulfur stretching frequency in these compounds and that observed in $K_2Hg(SCN)_4$ and the close agreement with the frequency observed in the thiocyanatocobalt ammines may well imply that a structure comparable to that proposed for $[Co(NH_3)_5NCS]Cl_2$ involving a double bond between the metal and the ligand exists in these polymeric materials. Further, the bridging by thiocyanate exhibited in these compounds should be quite analogous to that proposed by Werner for the silver adducts of the thiocyanatocobalt ammines.

The Structure of the Silver(I) Adducts.—1. The adduct of $(Co(NH_3)_5NCS]^{++}$, formed on the addition of a large excess of silver nitrate or silver perchlorate, does not analyze to be the 1:1 adduct proposed by Werner. Furthermore, the C–N and the C–S stretching frequencies are almost identical with those observed in the thiocyanatocobalt ammine ion itself. The potentiometric titration of thiocyanatopentamminecobalt(III) perchlorate with silver perchlorate gave no evidence for the formation of a stable compound in solution. Thus, no evidence for the formation of a silver—thiocyanatopentammine adduct was observed.

2. The adducts of both the *cis*- and *trans*-$[Co\ en_2(NCS)_2]^+$ are apparently real compounds involving a true bridging by thiocyanate. In both cases, the analysis of these adducts indicated a 1:1 compound, potentiometric titrations gave definite evidence for complex formation in solution, and the C–N stretching frequency in the *cis*-adduct is 27 cm.$^{-1}$ higher than that observed in the simple ion. This same shift in frequency to higher wave numbers is observed when the simple $K_2Hg(SCN)_4$ spectrum is compared with the spectra of bridged $MHg(SCN)_4$ compounds and is reported by Chatt and Duncanson[19] to be observed also in platinum compounds containing a thiocyanato bridge.

Assignment of N–H Vibrations in the Spectra of Bis-ethylenediaminecobalt Complexes.—Since the *cis*- and *trans*-bisthiocyanato-bisethylenediamine cobalt(III) thiocyanates are extremely resistant to aquation, these compounds were boiled with deuterium oxide and partial replacement of the labile hydrogens on the coördinated nitrogens obtained. On comparison of the spectra of the deuterated and undeuterated complexes, it appeared that the frequencies in the regions 3000–3300 cm.$^{-1}$, 1560–1600 cm.$^{-1}$, and 1120–1150 cm.$^{-1}$ could be attributed to various modes of N–H vibrations.

Further, it was observed that only one N–H vibration frequency appeared in the 1120–1150 cm.$^{-1}$ region in the *trans*-isomer but that two appeared in the *cis*-isomer. The differentiation between the *cis*- and *trans*-isomers also was observed in other bis-acido bis-ethylenediaminecobalt(III) complexes (Table III).

Acknowledgments.—The authors wish to express their appreciation to Dr. L. H. Jones of the Los Alamos Scientific Laboratories for instructing one of us (MMC) in the application of infrared spectroscopy to the solution of problems in inorganic chemistry and for helpful discussions; to Mr. James Brader for his work in obtaining the spectra reported herein; and to the National Science Foundation and the Socony-Mobil Oil Company for financial support.

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[17] S. B. Hendricks and H. E. Merwin, *Am. J. Sci.*, **15**, 487 (1928).

[18] J. W. Jeffery, *Nature*, **159**, 610 (1947).

[19] J. Chatt and L. A. Duncanson, *ibid.*, **178**, 997 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, UNIVERSITY OF SYDNEY]

Tridentate Chelate Compounds. II[1]

BY HAROLD A. GOODWIN[2] AND FRANCIS LIONS

RECEIVED MAY 12, 1959

A series of Schiff's bases has been prepared by condensing primary amines derived from pyridine or a benzpyridine with suitable aldehydes derived from pyridine or a benzpyridine. Their molecules contain three donor nitrogen atoms spaced similarly to the nitrogen atoms in the molecule of 2,6-bis-(α-pyridyl)-pyridine ("terpyridine"). Each has been shown to function as a tridentate with copper salts but it has been found that substituents adjacent to the donor nitrogen atom sequence lower the capacity of the organic molecule to coördinate with iron salts. 2,3,5,6-Tetrakis-(α-pyridyl)-pyrazine and 2,3,5,6-tetrakis-(6'-methyl-2'-pyridyl)-pyrazine with three-nitrogen sequences similar to that in terpyridine have also been synthesized. The former is an excellent tridentate. The coördinating capacity of the latter, especially with iron salts, appears to have been markedly lowered by the substituent methyl groups adjacent to the terminal nitrogen atoms of the three donor nitrogen atom sequence.

It was reported in Part I of this series of papers that 8-(α-pyridylmethyleneamino)-2-methylquinoline (Ia) was capable of forming coördination compounds with salts of metals such as iron (iron(II))

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[1] For Part I of this Series see F. Lions and K. V. Martin, THIS JOURNAL, **79**, 2733 (1957).

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