absorbance change associated with the second linear portion of Figure 3 is substantially larger than expected for any reaction of the monomeric products. The main reactions expected for the monomeric products in 1 *M* HCl is the conversion of *cis*-$Co(en)_2Cl_2^+$ and *cis*-$Co(en)_2(H_2O)Cl^{2+}$ to an equilibrium mixture of *cis*- and *trans*-$Co(en)_2(H_2O)Cl^{2+}$. From the known extinction coefficients and equilibrium constants[18] we estimate that these reactions of the monomers should account for only about 8% of the absorbance change at 525 mμ, whereas nearly 30% of the total absorbance change occurs after the first-order reaction of Figure 3 is complete. It must be admitted, however, that no direct evidence for the hypothetical chloride-bridged dimer has been obtained.

The formation of intermediate D has been written as a reversible reaction. If this reaction is irreversible, then it should be possible to use the increase and subsequent decrease in absorbance at 635 mμ to calculate the pseudo-first-order rate constants for the reaction scheme

$$\text{dimer} \xrightarrow{k_5} \text{D} \xrightarrow{k_6} \text{products}$$

where $k_5 = k_3[H^+][Cl^-]$. A reiterative computer fit[19] of the absorbance–time data at 635 mμ to such a scheme for consecutive first-order reactions gave $k_5 = 5.6 \times 10^{-2}$ sec^{-1} and $k_6 = 4.0 \times 10^{-2}$ sec^{-1} in 1 *M* HCl at 25°. From these values we calculate that the half-time for the production of products after the intermediate reaches steady state would be 23 sec, whereas a half-time of 21 sec for disappearance of the dimer is calculated from the data of Table IV. However, such a scheme also predicts a substantial induction period unless the reaction is followed at a wavelength such that the intermediate has an extinction coefficient similar to that of the product mixture. The rate of absorbance change at such a wavelength would of course yield the rate constant for the conversion of the dimer to the intermediate. The value of k, the first-order rate constant obtained from the absorbance change at 525 mμ where there is no induction period, is 2.98×10^{-2} sec^{-1} in 1 *M* HCl at 25° (see Table IV), which is substantially lower than the value $k_5 = 5.6 \times 10^{-2}$ sec^{-1}. This difference between k and k_5 may simply mean that the conversion of the dimer to the intermediate is after all a reversible reaction.

It cannot be claimed that the reaction of the dimer with HCl solutions is completely understood. However, it is at least clear from our observations that the dimer disappears in HCl solutions by a path involving the addition of one hydrogen ion and one chloride ion and that an intermediate which most likely is also dimeric and contains chloride is the immediate product of the diappearance of the dimer.

Since nitrato complexes were not found among the reaction products and since the behavior of the dimer in nitrate solutions was qualitatively similar to that in perchlorate solutions, there is no basis for ascribing a role to nitrate similar to that ascribed to chloride. The effect of nitrate on the parameter a (k_1 of the proposed mechanism) is not unreasonably large for a salt effect when the 4+ charge of the dimer and the 4+ and 5+ charges of the proposed intermediates are considered.

There is a drastic difference between the behavior of $(en)_2Co(OH)_2Co(en)_2^{4+}$ and that of $(en)_2Cr(OH)_2Cr(en)_2^{4+}$ in cleavage reactions. The chromium(III) complex cleaves at a rate independent of $[H^+]$ in perchlorate solutions but is subject to very effective nitrate-catalyzed cleavage, the cleavage rate in 1 *M* HNO_3 being *ca.* 100 times that in 1 *M* $HClO_4$.[20]

Acknowledgment.—The authors are grateful to the National Science Foundation for support of this research through Grants GP-5425 and GP-9115.

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(18) M. E. Baldwin, S. C. Chan, and M. L. Tobe, *ibid.*, 4637 (1961).

(19) K. B. Wiberg, "Computer Programming for Chemists," W. A. Benjamin, New York, N. Y., 1965, p 181.

(20) NOTE ADDED IN PROOF.—Results of an independent kinetic study of the reaction of the dimer in $HClO_4$ solutions have been reported recently: A. A. El-Awady and Z Z. Hugus, Jr., *Inorg. Chem.* **10**, 1415 (1971).

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Metal Chelates Containing Bicyclic Rings. II. Preparation and Characterization of Hydroxymethylenenorcamphor and Its Metal Chelates

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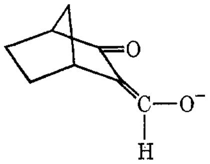
A new ligand, hydroxymethylenenorcamphor (HMNC), has been synthesized and characterized. Several new $HMNC^-$ chelates have been prepared from the first transition series metals. These compounds are the simplest members of a class of chelates in which a bicyclic-ring system is fused to an unsaturated, six-membered chelate ring. The infrared spectra indicate a significant chelate ring asymmetry due to the presence of the strained five-membered ring fused to it. Magnetic, molecular weight, and analytical data indicate that several of the bis chelates exist as oligomeric molecules containing bridging oxygens from chelated $HMNC^-$.

Introduction

Chelates in which an anionic, bidentate ligand contains a bicyclic-ring system are not well known. The only compounds of this type previously reported contain the camphor group. Certain features have prompted us to investigate a number of chelates containing bicyclic groups, including the camphor group. These features are as follows: (1) optically pure ligands are obtainable in many cases, (2) there are readily variable structural features in the bicyclic-ring system, and (3) the electronic structure of the chelate ring can be significantly modified by changing the size of the bicyclic ring system fused to it.

Several old, and a few recent, investigations of hydroxymethylenecamphorate (HMC^-) chelates have been reported.[1-14] Most of these papers are concerned with some aspect of optical studies and stereoselective coordination. Our first paper in this series[14] deals with the synthesis and characterization of several new chelates of HMC^-, the electronic situation in the chelate ring, and oligomer formation in the divalent bis chelates.

The subjects of this paper are the syntheses and characterizations of chelates containing the anionic ligand hydroxymethylenenorcamphorate ($HMNC^-$), shown below. To our knowledge neither the ligand



nor the chelates have been reported previously. Preparation of the optically pure isomers of $HMNC^-$ should prove interesting in the study of stereoselective coordination. Several workers[6,10] have reported stereoselective coordination in the tris chelates of HMC^-. Dunlap, Gillard, and Ugo[6] have discussed the possibility that the stereoselectivity is due to the steric interaction of the methyl groups on the camphor ring. Optical studies using tris chelates made from optically pure $HMNC^-$ will test this theory since the methyl groups in HMC^- are replaced by hydrogen atoms in $HMNC^-$. The optically pure isomers of HMNC have not as yet been prepared.

Experimental Section

Hydroxymethylenenorcamphor.—A mixture of 45 g of potassium *tert*-butoxide and 300 ml of dry ether was placed in a 1000-ml three-necked flask. The flask was fitted with a stirrer, a condenser, and a dropping funnel. The mixture was chilled with an ice bath. The entire system was continually flushed with dry nitrogen. A solution of 12.0 g (0.11 mol) of norcamphor and 55 ml (0.41 mol) of pentyl formate in 300 ml of dry ether was placed in the dropping funnel. Addition time was about 1 hr. This mixture was allowed to stir overnight without further cooling. The resulting orange-yellow reaction mass was dissolved in 300 ml of ice water. The ether and water layers were separated and the water layer was washed with three 50-ml portions of ether. The ether layers were discarded. The water layer was chilled and acidified with a 50:50 HCl–water solution. The product was extracted into about 100 ml of ether. The water and ether layers were separated and the ether layer was saturated with an NaCl solution, after which it was dried over $MgSO_4$. The ether was removed under vacuum and the product was vacuum distilled. Hydroxymethylenenorcamphor (HMNC) is a clear, viscous liquid that boils at 87° under vacuum pump pressure (*ca.* 0.1 mm). The product slowly decomposes in the atmosphere to an extremely viscous, yellow liquid which appears to be an organic acid. For this reason the product was sealed under vacuum and used soon after preparation. *Anal.* Calcd for $C_8H_{10}O_2$: C, 69.57; H, 7.25. Found: C, 69.65; H, 7.45.

$Cu(HMNC)_2$.—A ligand solution was prepared by dissolving 2.0 g (0.015 mol) of HMNC in about 50 ml of methanol. A second solution containing 1.7 g (0.0075 mol) of cupric acetate monohydrate in a minimum amount of methanol was prepared in a separate beaker. The crude product was formed by adding the ligand solution to the Cu(II) solution. The methanol was allowed to evaporate, yielding a green oil. The oil was dissolved in about 50 ml of heptane. The heptane solution was concentrated to about 20 ml. A small amount of petroleum ether (bp 37–55°) was added and the solution was cooled to about 0° in a refrigerator. A bright green powder formed on cooling. This product was collected, air-dried, and recrystallized from heptane. The chelate melts at 145°. Attempts at chromatographic purification using alumina or sucrose columns resulted in decomposition of the product. *Anal.* Calcd for $Cu(C_8H_9O_2)_2$: C, 56.9; H, 5.33; Cu, 18.8. Found: C, 56.8; H, 5.76; Cu, 19.0.

$Co(HMNC)_2 \cdot 0.5H_2O$.—A solution of 1.0 g (0.0073 mol) of HMNC in 25 ml of methanol was added to an excess of cobaltous acetate dissolved in water. A pink precipitate formed immediately. The precipitate was collected, washed several times with an 80% methanol–water solution, and vacuum dried. The product was washed repeatedly by extraction with acetone in a Soxhlet extractor. The infrared spectrum and the analysis proved the presence of water in the product. The pink powder does not melt up to 300° and is not soluble in most organic solvents or water. *Anal.* Calcd for $Co(C_8H_9O_2)_2 \cdot 0.5H_2O$: C, 56.1; H, 5.55; Co, 17.2. Found: C, 56.1; H, 5.47; Co, 16.9.

$Ni(HMNC)_2 \cdot 0.25H_2O$.—This chelate was prepared in the same manner as $Co(HMNC)_2 \cdot 0.5H_2O$. The light green powder does not melt up to 300° and is not soluble in most organic solvents or water. *Anal.* Calcd for $Ni(C_8H_9O_2) \cdot 0.25H_2O$: C, 56.9; H, 5.48; Ni, 17.3. Found: C, 56.8; H, 5.67; Ni, 17.0.

$Mn(HMNC)_2 \cdot 2H_2O$.—A solution of 6.9 g (0.05 mol) of the ligand in 100 ml of methanol was added to a solution of 4.85 g (0.025 mol) of $MnCl_2 \cdot 4H_2O$ in 250 ml. Exposure to the atmosphere and heat was kept at a minimum. A solution of 6.8 g (0.05 mol) of sodium acetate in 150 ml of water was added slowly, followed by 5.25 ml of concentrated aqueous ammonia. This solution was stirred for 10 min and placed in a refrigerator for several hours. The yellow product that precipitated was filtered, washed with a cold methanol–water mixture, and dried under vacuum at room temperature. It decomposes to a light tan compound upon exposure to air. The freshly prepared sample is not soluble in water or in most common organic solvents. It decomposes at 150°. *Anal.* Calcd for $Mn(C_8H_9O_2)_2 \cdot 2H_2O$: C, 52.6; H, 6.03; Mn, 15.1. Found: C, 53.3; H, 5.27; Mn, 15.9.

$Zn(HMNC)_2$.—This compound was prepared in a manner similar to $Co(HMNC)_2 \cdot 0.5H_2O$. The white powder is not soluble in water or in common organic solvents. The infrared spectrum substantiates the anhydrous formulation. The compound does not melt but begins to decompose at 290°. *Anal.* Calcd for $Zn(C_8H_9O_2)_2$: C, 56.6; H, 5.21; Zn, 19.1. Found: C, 56.3; H, 5.67; Zn, 19.6.

$Co(HMNC)_3$.—The method used to prepare this complex is basically that of Dunlap, Gillard, and Ugo[6] with some modification. A solution of 2.0 g (0.015 mol) of the ligand in 50 ml of benzene was added to a mixture of 1.8 g (0.005 mol) of $Na_3[Co(CO_3)_3] \cdot 3H_2O$ in 50 ml of water. The mixture was stirred vigorously. After a short time, a red color developed in the water layer indicating the presence of Co(II) species. To prevent this, small amounts of nitric acid and hydrogen peroxide were added. The mixture was stirred for 12 hr. Then the green benzene layer was separated from the pink water layer. The benzene layer was concentrated to about 20 ml, placed directly on an alumina column, and eluted with acetone. The resulting solution was evaporated to dryness. The product was dissolved in boiling petroleum ether (bp 37–55°) and then precipitated on cooling. The yellow-green product melts at 106° and turns to a red liquid at 140°. It is soluble in most common organic solvents. *Anal.* Calcd for $Co(C_8H_9O_2)_3$: C, 61.3; H, 5.74. Found: C, 61.4; H, 6.43.

$Cr(HMNC)_3$.—All the standard Cr(III) preparations which

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(1) A. W. Bishop, L. Claisen, and W. Sinclair, *Ann.*, **281**, 314 (1894).

(2) J. Lifshitz, *Recl. Trav. Chim. Pays-Bas*, **41**, 627 (1922).

(3) J. Lifshitz, *Z. Phys. Chem., Stoechiom. Verwandschaftslehre*, **105**, 27 (1923).

(4) P. Pfeiffer, W. Christelheit, T. Hesse, H. Pfitzner, and H. Theilert, *J. Prakt. Chem.*, **150**, 261 (1938)

(5) D. P. Mellor, *J. Proc. Roy. Soc. N. S. W.*, **75**, 157 (1942).

(6) J. H. Dunlap, R. D. Gillard, and R. Ugo, *J. Chem. Soc. A*, 1540 (1966).

(7) Y. T. Chen and G. W. Everett, *J. Amer. Chem. Soc.*, **90**, 6660 (1968).

(8) C. R. Powers and G. W. Everett, *ibid.*, **91**, 3468 (1969).

(9) C. S. Springer, R. E. Sievers, and B. Feibush, presented to the 157th Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

(10) J. Lifshitz, *Recl. Trav. Chim. Pays-Bas*, **69**, 1495 (1950).

(11) R. E. Ballard, A. J. McCaffery, and S. F. Mason, *Proc. Chem. Soc.*, 331 (1962).

(12) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965).

(13) G. W. Everett and C. R. Powers, *Inorg. Chem.*, **9**, 521 (1970).

(14) R. L. Lintvedt and A. M. Fatta, *ibid.*, **7**, 2489 (1968).

involve Cr(II) ⇌ Cr(III) equilibria[15] gave a variety of products, including Cr(III) species in which the ligand was oxidized. Purification of the crude product prepared by the method of Collman and Kittleman was attempted by recrystallization and column chromatography using various absorbents. The great solubility of the complex in organic solvents rendered recrystallizations useless. Column separations were inefficient. The complex decomposed on columns packed with strong absorbents. The best fraction contained ligand impurity but does have a sharp, well-defined infrared spectrum in which the ligand absorptions are present. Analyses for three isolated products are given below.

Anal. Calcd for $Cr(C_8H_9O_2)_3$: C, 61.8; H, 5.8; Cr, 11.2. Found: C, 63.9; H, 6.61; Cr, 12.0. Calcd for $Cr(C_8H_{10}O_3)_3$: C, 56.4; H, 6.28. Found: C, 56.1; H, 5.17. Calcd for $Cr(HMNC)_2(H_2O)(OH)$: C, 53.2; H, 5.8. Found: C, 52.3; H, 5.82. The first complex has a very low melting point, indicating ligand impurity. The second, $Cr(C_8H_{10}O_3)_3$, melts at 120°. The third, $Cr(C_8H_9O_2)_2(H_2O)(OH)$, melts at 190°.

Fe(HMNC)$_3$.—The difficulties encountered in the Cr(III) complex were encountered in the preparation and purification of $Fe(HMNC)_3$ as well. The preparative method employed was a modification of the method used to prepare $Co(HMNC)_3$. The tris(carbonato)iron(III) complex was prepared in exactly the same manner as the analogous Co(III) compound. It is quite unstable and must be used immediately. The extreme solubility of the product in all common organic solvents precludes purification by recrystallization. All common absorbents except lactose decompose the compound. Separation of the product and the ligand after repeated elusions on lactose columns was incomplete. Analysis and infrared spectra indicated ligand impurity. *Anal.* Calcd for $Fe(C_8H_9O_2)_3$: C, 61.7; H, 5.78. Found: C, 62.8; H, 6.37.

Co(HMNC)$_2$(py)(H$_2$O).—A sample of $Co(HMNC)_2 \cdot 0.5H_2O$ was dissolved in a small amount of pyridine. No attempt was made to dry the pyridine. The resulting yellow-orange solution was evaporated to dryness and the product was dried under vacuum. The analysis is shown below. Both the analysis and the infrared spectrum indicate that water is still present. Attempts to displace the water by continuous extraction with hot pyridine in a Soxhlet extractor yielded a product identical with the original pyridine adduct. The orange-brown compound loses pyridine at 150° at which point it turns red. It does not melt up to 300°. *Anal.* Calcd for $Co(C_8H_9O_2)_2(C_5H_5N)(H_2O)$: C, 58.6; H, 5.81. Found: C, 58.9; H, 5.62.

Ni(HMNC)$_2$(py)·0.5H$_2$O.—The pyridine adduct of $Ni(HMNC)_2) \cdot 0.25H_2O$ was prepared in the same manner as the Co(II) adduct. The presence of water is indicated by analysis and by the infrared spectrum. The light green product did not melt or appear to lose pyridine up to 300°. *Anal.* Calcd for $Ni(C_8H_9O_2)_2(C_6H_5N] \cdot 0.5(H_2O)$: C, 59.9; H, 5.70. Found: C, 60.0; H, 5.61.

Nuclear Magnetic Resonance Spectra.—Nmr spectral data reported were recorded with a Varian A-60 nmr spectrometer. The solvent was carbon tetrachloride. The spectra were calibrated *vs.* TMS (chemical shift 0). All spectra were obtained using freshly distilled HMNC.

Infrared Spectral Measurements.—All infrared spectra were recorded on a Perkin-Elmer Model 621 spectrophotometer. The ligand spectrum was run neat and all chelates were run as KBr pellets. The spectra were calibrated in the 2850-, 1600-, and 900-cm^{-1} regions using appropriate polystyrene absorptions.

Molecular Weight Determination.—Molecular weights were determined cryoscopically in camphor. A mixture of known molality was prepared and melted to ensure intimate mixing. After cooling, the melting point of the solid mixture was observed. The capillary tubes used to hold the sample were sealed as close as possible to the solid mixture so as to minimize sublimation of camphor before melting. Typical melting point depressions for mixtures used were 5–6°.

Magnetic Susceptibility Measurements.—Magnetic moments were determined using standard Gouy method techniques. The complex $Hg[Co(NCS)_4]$ was used as a calibrant. The results have been corrected for the diamagnetic effect of the ligands.

pK_a Measurement.—The pK_a of the ligand was determined titrametrically with a Sargent pH meter, Model DR, and calomel electrodes.

Results

Nuclear Magnetic Resonance Spectra.—The spectrum of freshly distilled HMNC contains absorptions assignable to both keto and enol forms. Only the low-field spectrum of protons on and near the oxygens will be discussed here. An absorption at 5.58 ppm is assigned to the aldehyde proton in the hydrogen-bonded enolic form of HMNC. A concentration-dependent broad band which occurs from about 6 to 7 ppm is assigned to the alcoholic proton in the enol. No absorption was observed downfield which could be attributed to a strongly hydrogen-bonded proton. The peak may have escaped detection, however, due to low intensity and extreme broadness. In any case it is clear that the intramolecular hydrogen bonding in HMNC is not as important as in the camphor analog.[14] Two very sharp absorptions of nearly equal intensity at 9.63 and 9.75 ppm are assigned to the exo and endo aldehyde proton in the keto form.

pK_a Determination.—The pK_a of HMNC was determined by standard titrametric techniques. A sodium hydroxide solution was standardized by titration with potassium acid phthalate. Ligand solutions 0.005 *M* in HMNC and 0.1 *M* in $NaClO_4$ were prepared with a 65% water–methanol mixture. These solutions were titrated with the standardized base solution. The pH of a 0.00481 *M* HMNC solution in 65% water–methanol is 4.80 at 25°. From the halfway point in the titration the pK_a was determined to be 7.33. These results were obtained on freshly prepared, freshly distilled samples of HMNC. Samples allowed to age become more acidic. This substantiates other observations which indicate the ligand decomposes on standing by oxidation to the acid.

Infrared Spectra.—The infrared spectra of HMNC and norcamphor were compared so that organic group absorption could be detected and assigned in the chelates of HMNC. Absorptions characteristic of the 1,3-diketone system in HMNC are as follows. A strong, broad band between 3700 and 3000 cm^{-1} is assigned to the hydrogen-bonded OH stretch. Aldehydic C—H stretching and deformation occur at 2810 and 2750 cm^{-1}. The strong C=O stretch appears at 1725 cm^{-1}. A strong peak at 1618 cm^{-1} is assigned to a C=C stretching frequency in the enolic form.

The following results summarize the pertinent information obtained from the infrared spectra of the HMNC chelates.

1800–1200-Cm^{-1} Region.—This region of the chelate spectra contains the three strongest bands. The highest frequency absorption (1660–1600 cm^{-1}) is assigned to a relatively pure chelated $C\overset{\cdots}{-}O$ stretch. The second intense band is assigned to the $C\overset{\cdots}{-}C$ stretch in the chelate ring. It occurs between about 1475 and 1520 cm^{-1}. The third strong band (1300–1320 cm^{-1}) is assigned to another $C\overset{\cdots}{-}O$ vibration. These assignments agree very well with the assignments made previously for the hydroxymethylenecamphor (HMC) chelates.[14] The separation between the two C–O vibrations is between 300 and 355 cm^{-1} The position of these absorptions and the energy separations between them are, as expected, functions of the metal ion.

1200–800-Cm^{-1} Region.—Most absorptions in this region are characteristic of the ligand and will not be discussed further. A relatively strong band near 1200

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(15) See, for example, J. P. Collman and E. T. Kittleman, *Inorg. Syn.*, **8**, 149 (1966).

TABLE I

ABBREVIATED INFRARED SPECTRA OF HMNC CHELATES IN THE 1800–300-CM^{-1} REGION (AS SOLIDS IN KBr PELLETS)[a]

Cu(II)	Zn(II)	Mn(II)	Ni(II)	Ni(II)[b]	Co(II)	Co(II)[b]	Co(III)	Cr(III)	Fe(III)	Intens[c]	Assignment
1630	1655	1653	1647	1641	1645	1640	1611	1618	1616	s	C–O str
1507	1510	1510	1498	1521	1503	1515	1478	1495	1493	s	C–C str
1318	1300	1299	1305	1298	1310	1305	1317	1320	1303	s	C–O str
1205	1198	1195	1195	1196	1198	1195	1210	1212	1214	s	C–C str
1097	1099	1097	1097	1098	1098	1098	1102	1105	1103	s	Ring def
733	734	730	731	732	731	732	739	736	740	m	Aldehyde C–H bending
697	695	691	693	698	693	700 sh	704	701	697	m	
603	610	607	608	624	608	625	618	609	604	w	
555	511	500	523	515	513	511	573	542	500	m	M–O str

[a] Only absorptions pertinent to the discussion have been included. [b] These chelates are the ppridine adducts. [c] Key: s, strong; m, medium; w, weak.

cm^{-1} is dependent on the metal ion and is assigned to a C–C vibration in the chelate ring. Several of the "ligand" absorptions have relative intensities which are a function of the metal ion and its oxidation state.

800–300-Cm^{-1} Region.—Three absorptions between 600 and 740 cm^{-1} occur virtually unshifted in all the chelates. Since these peaks are not present in the ligand and are relatively insensitive to changes in the metal ion, it is reasonable to assign them to chelated aldehydic C–H bending frequencies. Similar observations have been made on the chelates of the camphor analog.[14] A peak of medium intensity in the 500–600-cm^{-1} region is strongly dependent on the metal ion and probably consists of relatively pure M–O stretching.

Absorptions of importance are presented in Table I. Several absorptions that are characteristic of the bicyclic group have been omitted for the sake of clarity.

Magnetic Studies.—The magnetic moment of Co(HMNC)$_2\cdot$0.5H$_2$O is 4.97 BM at 296°K, which indicates a high-spin octahedral complex with a $^4T_{1g}$ ground state. The magnetic moment of Ni(HMNC)$_2\cdot$0.25H$_2$O is 3.05 BM at 296°K which is characteristic of octahedral coördination with an $^4A_{2g}$ ground state. The magnetic results show that these complexes are not simple but most likely exist as oligomers similar to the camphor analogs.[14]

Molecular Weight and Analytical Results.—Cryoscopic molecular weight determinations were carried out in camphor on the Ni(II) and Co(II) chelates. These data complement the magnetic measurements by proving the oligometric nature of the complexes. The measured molecular weight for the complex Co(HMNC)$_2\cdot$0.5H$_2$O is 666. The theoretical molecular weight for the dimer Co$_2$(HMNC)$_4$(H$_2$O) is 684. The measured molecular weight for Ni(HMNC)$_2$.0.25H$_2$O is 1333. The theoretical molecular weight for the tetramer Ni$_4$(HMNC)$_8$(H$_2$O) is 1350. The analytical results of these M(II) chelates are understandable in view of their oligomeric nature. The unusual numbers of water molecules result from a best fit for the analytical data. The fractional representation is due to water molecules filling available coordination sites on the oligomeric molecule. The belief that the water molecules are coordinated to the metal is strongly supported by our inability to remove them by extraction with acetone or by heating. Removal by strong heating results in decomposition.

Discussion

The ligand and chelates discussed herein have not been previously reported. These chelates represent the simplest members of a class of compounds that contain a bicyclic-ring system fused to an unsaturated, six-membered chelate ring. The ligand HMNC$^-$ is a clear, viscous liquid which is quite susceptible to air oxidation. Oxidation to the corresponding acid is relatively complete in a few days of atmospheric exposure. The acid can act as an anionic, bidentate ligand as well. Chelates of this acid have been identified, *e.g.*, Cr(C$_8$H$_{10}$O$_3$)$_3$. The oxidation of HMNC makes it necessary to synthesize the chelates from a freshly prepared, freshly distilled sample. In addition, chelation syntheses involving oxidative conditions must be avoided.

Separation of optically pure isomers of HMNC has been attempted using optically active amines. These attempts were unsuccessful, however, due to the formation of the corresponding 1,3-keto imines. These potentially interesting imine-type ligands are easily prepared crystalline compounds. Imines have been made from the following optically active amines: amphetamine, resoline, ephedrine, phenylethylamine, bruccine, and cinchonine. Isolation of optically pure HMNC is of interest because of the reported stereoselective coordination of its camphor analog, HMC$^-$.[6,10] If the methyl groups of HMC$^-$ cause stereoselectivity,[6] then HMNC$^-$ will not coordinate stereoselectively. All structural aspects of the two chelates should be identical except for the absence of the three camphor methyl groups in HMNC$^-$.

The infrared spectra of the HMNC$^-$ chelates are identical in all major aspects with the spectra of the HMC$^-$ chelates.[14] In the present case, as well as in the HMC$^-$ chelates, the relatively large energy separation between the chelate ring C–O stretching frequencies is taken as evidence for a somewhat unsymmetric chelate ring.[14,16] The asymmetry is presumably due to the strained five-membered ring fused to the chelate ring.

The formulations showing varying numbers of water molecules per metal atom for several bis chelates are not considered to be analytically proven. However, the results of at least three different types of measurements can be rationalized by them. First, the elemental analyses are consistent with the formulas as written and the infrared spectra indicate the presence of water. Second, the magnetic moments for the bis chelates of Ni(II) and Co(II) are typical for octahedral coordination in both cases. With only two chelating ligands present, the remaining coordination sites are taken by water molecules. Third, the molecular weights of the bis chelates of Ni(II) and Co(II) can be

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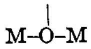
(16) G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 433 (1967).

explained by oligomerization. Similar observations were made for the HMC$^-$ chelates.[14] It is most likely that the oligomers contain HMNC$^-$ oxygens that are coordinated to two metals, thereby forming an


$\mathrm{M{-}\overset{|}{O}{-}M}$

bridging system. The remaining octahedral coordination sites, *i.e.*, those not containing either bridging or nonbridging HMNC$^-$ oxygens, are taken by water molecules. Hence, fractional numbers of water molecules per metal atom are the result of the number of bridge bonds formed, or in other words, of the structure of the oligomeric molecule. For $Co(HMNC)_2 \cdot 0.5H_2O$, the structure which is consistent with all these data is a dimer, $Co_2(HMNC)_3(H_2O)$, containing a shared face between two basically octahedral units. The twelve coordination sites are filled by five nonbridging HMNC$^-$ oxygens, three bridging HMNC$^-$ oxygens, and one oxygen from a water molecule. For $Ni(HMNC)_2 \cdot 0.25H_2O$, the structure which is consistent with all these data is a tetramer, $Ni_4(HMNC)_8(H_2O)$, containing two shared edges and a shared face between four basically octahedral units. The twenty-four coordination sites are filled with nine nonbridging HMNC$^-$ oxygens, seven bridging HMNC$^-$ oxygens, and one oxygen from a water molecule. On the basis of structures such as these, the presence of water is understandable. It must be present to complete the pseudooctahedral coordination of all the metal ions. Furthermore, our inability to remove the water molecule can be explained, since removal without decomposition would require extensive molecular rearrangement.

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Kinetics of the Spontaneous Aquation and Linkage Isomerization of the S-Bonded–N-Bonded Dithiocyanate Complex of Chromium(III)

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A novel complex ion of chromium(III) containing two thiocyanate ions, one S bonded and the other N bonded, has been prepared in solution by the reaction of Fe*N*CS^{2+} with Cr^{2+}(aq) in the presence of free thiocyanate ion. The complex ion undergoes two spontaneous reactions, aquation and linkage isomerization, both involving the S-bonded ligand. The rate law has the form: rate = $(k_0 + k_{-1}/[H^+])[Cr(\mathit{S}CN)(\mathit{N}CS)^+]$, where $k_0 = k_0^a + k_0^i$ and $k_{-1} = k_{-1}^a + k_{-1}^i$. The rate constants at 25.0° and $\Sigma[ClO_4^-] = 1.0\ M$ followed by the enthalpies (kcal/mol) and entropies (eu) of activation in parentheses are as follows: $k_0^a = 1.09 \times 10^{-4}$ sec^{-1} (19.6, −9.8), $k_0^i = 8.3 \times 10^{-5}$ sec^{-1} (19.6, −9.8), $k_{-1}^a = 7.3 \times 10^{-6}\ M$ sec^{-1} (24.9, 2.6), and $k_{-1}^i = 5.5 \times 10^{-6}\ M$ sec^{-1} (24.9, 2.6) in the ranges 18.0–34.5° and 0.10–1.00 M H$^+$.

Introduction

In the last ten years there has been considerable interest in the study of linkage isomerism involving the thiocyanate ion.[1-7] However, there have been relatively few examples of thiocyanate complexes containing both bonding modes. These are Pd(Me$_2$bipy)(*S*CN)(*N*CS),[8] Cu(tripyam)(*S*CN)(*N*CS),[9] Pd[$(C_6H_5)_2$As(*o*-C_6H_4)P-$(C_6H_5)_2$](*S*CN)(*N*CS),[10] $M_2[(C_6H_5)_2PC_2P(C_6H_5)_2]_2$-(*S*CN)(*N*CS),[11] where M = Pd(II) and Pt(II), and Pd[$(C_6H_5)_2P(CH_2)_3N(CH_3)_2$](*S*CN)(*N*CS).[12] The last example is particularly noteworthy since the X-ray crystal structure study[12] unequivocally establishes that one thiocyanate ion is S bonded while the other is N bonded. One other related example[13] involves a binuclear complex of platinum(II) containing two bridging thiocyanate ions such that each platinum(II) ion has one S-bonded and one N-bonded thiocyanate ion.

The present study presents evidence for the formation and characterization of an S-bonded–N-bonded dithiocyanate complex ion of chromium(III), $Cr(OH_2)_4$-(*S*CN)(*N*CS)$^+$, in solution. The kinetics of the spontaneous aquation and linkage isomerization of $Cr(OH_2)_4$-(*S*CN)(*N*CS)$^+$ are also reported. The latter reactions parallel very closely those observed for $Cr(OH_2)_5$-*S*CN^{2+}.[2,4]

Experimental Section

Materials.—Chromium(II) solutions were prepared by reduction of chromium(III) perchlorate in 0.1 M perchloric acid with lightly amalgamated zinc. The reduction was carried out in an oxygen-free container through which prepurified argon was passed. The argon used was passed through a heated copper catalyst (BASF) at 120° to remove traces of oxygen. The chromium(II) solutions were stored under an argon atmosphere in serum bottles capped with self-sealing rubber stoppers.

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(1) See for example ref 10–26, 34, and 35 in J. L. Burmeister, *Coord. Chem. Rev.*, **3**, 225 (1968).

(2) A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, **87**, 4210 (1965); **88**, 434 (1966).

(3) B. R. Baker, M. Orhanović, and N. Sutin, *ibid.*, **89**, 722 (1967).

(4) M. Orhanović and N. Sutin, *ibid.*, **90**, 538, 4286 (1968).

(5) M. Orhanović, H. N. Po, and N. Sutin, *ibid.*, **90**, 7224 (1968).

(6) D. A. Buckingham, I. I. Creaser, and A. M. Sargeson, *Inorg. Chem.*, **9**, 655 (1970).

(7) D. P. Fay and N. Sutin, *ibid.*, **9**, 1291 (1970).

(8) I. Bertini and A. Sabatini, *ibid.*, **5**, 1025 (1966).

(9) G. C. Kulasingam and W. R. McWhinnie, *Chem. Ind.* (*London*), 2200 (1966).

(10) P. Nicpon and D. W. Meek, *Inorg. Chem.*, **6**, 145 (1967).

(11) A. J. Carty and A. Efraty, *Can. J. Chem.*, **47**, 2573 (1969).

(12) G. R. Clark, G. J. Palenik, and D. W. Meek, *J. Amer. Chem. Soc.*, **92**, 1077 (1970).

(13) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1416 (1961).