were changed and least-squares refinement was continued. R_F and R_{wF} dropped to their final values and a better value for the error in an observation of unit weight (1.236 vs. 1.252) was obtained. Thus, the second enantiomorph was deemed to be the correct one. A final difference Fourier was now featureless. Crystallographic data for the untwinned crystal are given in Table III.

All programs used in the refinement were part of the Enraf-Nonius structure determining package.[34] Positional and anisotropic temperature factors for all the atoms are given in Table X; bond distances and angles in Tables XI and XII, respectively. Equations of least-squares planes are given in Table XIII. Tables of observed and calculated structure factors are available; see paragraph at end of paper and also ref 35.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. We are also indebted to Dr. John Fleming of the Perkin-Elmer Corp. for assistance in obtaining the variable-temperature ^{1}H NMR spectra. I.B. and G.M.R. thank the U.S. National Science Foundation for providing funds to purchase the diffractometer, the Robert A. Welch Foundation for research grants, and the Computer Center of the University of Houston for a generous supply of free computing time.

Registry No. **1**, 12078-25-0; **3**, 29778-31-2; **4**, 5806-58-6; **5**, 1278-02-0; **6**, 70749-43-8; **8**, 70775-26-7; iodomesitylene, 4028-63-1; cuprous phenylacetylide, 13146-23-1.

Supplementary Material Available: A listing of structure factor amplitudes for compound **6** (10 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) University of Massachusetts. (b) University of Houston. (c) Texas A&M University. (d) Molecular Structure Corp.
(2) M. D. Rausch and R. A. Genetti, *J. Org. Chem.*, **35**, 3888 (1970).
(3) M. D. Rausch, Fifth International Conference on Organometallic Chemistry, Moscow, USSR, Aug. 16–21, 1971, Abstracts of Plenary & Section Lectures, Vol. III, p 10; *Pure Appl. Chem.*, **30**, 523 (1972).
(4) I. Bernal, B. R. Davis, M. D. Rausch, and A. Siegal, *J. Chem. Soc., Chem. Commun.*, 1169 (1972).
(5) M. D. Rausch, I. Bernal, B. R. Davis, A. Siegal, F. A. Higbie, and G. F. Westover, *J. Coord. Chem.*, **3**, 149 (1973).
(6) A. Clearfield, R. Gopal, M. D. Rausch, E. F. Tokas, F. A. Higbie, and I. Bernal, *J. Organomet. Chem.*, **135**, 229 (1977).
(7) M. D. Rausch, S. A. Gardner, E. F. Tokas, I. Bernal, G. M. Reisner, and A. Clearfield, *J. Chem. Soc., Chem. Commun.*, 187 (1978).
(8) M. D. Rausch, F. A. Higbie, G. F. Westover, A. Clearfield, R. Gopal, J. M. Troup, and I. Bernal, *J. Organomet. Chem.*, **149**, 245 (1978).
(9) S. A. Gardner, E. F. Tokas, and M. D. Rausch, *J. Organomet. Chem.*, **92**, 69 (1975).
(10) S. A. Gardner and M. D. Rausch, *J. Organomet. Chem.*, **78**, 415 (1974).
(11) R. G. Gastinger, M. D. Rausch, D. A. Sullivan, and G. J. Palenik, *J. Am. Chem. Soc.*, **98**, 719 (1976).
(12) R. G. Gastinger, M. D. Rausch, D. A. Sullivan, and G. J. Palenik, *J. Organomet. Chem.*, **117**, 355 (1976).
(13) H. Yamazaki and N. Hagihara, *J. Organomet. Chem.*, **21**, 431 (1970).
(14) H. Yamazaki and Y. Hagihara, *J. Organomet. Chem.*, **139**, 157 (1977).
(15) K. P. C. Vollhardt, *Acc. Chem. Res.*, **10**, 1 (1977).
(16) W. S. Lee and H. H. Brintzinger, *J. Organomet. Chem.*, **127**, 93 (1977).
(17) G. B. Kaufmann and R. P. Pinnell, *Inorg. Synth.*, **6**, 3 (1960).
(18) C. E. Castro, E. J. Gaughan, and D. C. Owsley, *J. Org. Chem.*, **31**, 4071 (1966).
(19) C. H. Bushweller, G. Bhat, L. J. Letendre, J. A. Brunell, H. S. Biloffsky, H. Ruben, D. H. Templeton, and A. Zalkin, *J. Am. Chem. Soc.*, **97**, 65 (1975).
(20) H. E. Zimmerman and J. R. Dodd, *J. Am. Chem. Soc.*, **92**, 6507 (1970).
(21) P. E. Riley and R. E. Davis, *J. Organomet. Chem.*, **113**, 157 (1976).
(22) A. C. Villa, L. Coghi, A. Manfredotti, and C. Guastini, *Acta Crystallogr., Sect. B*, **30**, 2101 (1974).
(23) C. Kabuto, J. Hayashi, H. Sakurai, and Y. Katahara, *J. Organomet. Chem.*, **43**, C23 (1972).
(24) C. H. Saldarriaga-Molina, A. Clearfield, and I. Bernal, *Inorg. Chem.*, **13**, 2880 (1974), and references cited therein.
(25) W. Bunder and E. Weiss, *J. Organomet. Chem.*, **92**, 65 (1975).
(26) R. M. Tuggle and D. L. Weaver, *Inorg. Chem.*, **10**, 1504 (1971).
(27) R. Allmann and E. Helmer, *Chem. Ber.*, **101**, 2522 (1968).
(28) (a) G. M. Reisner, I. Bernal, H. Brunner, and J. Wachter, *J. Organomet. Chem.*, **137**, 329 (1977); (b) G. M. Reisner, I. Bernal, H. Brunner, and M. Muschiol, *Inorg. Chem.*, **17**, 738 (1978); (c) G. M. Reisner, I. Bernal, and G. R. Dobson, *J. Organomet. Chem.*, **157**, 23 (1978).
(29) J. M. Stewart, G. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall, Eds., "The X-Ray System of Crystallographic Programs", Technical Report No. 192, Computer Science Center, University of Maryland, 1972.
(30) D. Cromer and J. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
(31) R. F. Stewart, E. R. Davison, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(32) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1967, p 215.
(33) C. K. Johnson, "ORTEP2, A Fortran-Ellipsoid Plot Program for Crystal Structure Illustration", ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1972.
(34) ENRAF-NONIUS, Structure Determination Package (SDP), Delft, Holland, 1975; revised 1977.
(35) Tables of structure factors have been deposited as NAPS document No. 03512 with NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document and remitting $3.00 for microfiche and $5.00 for photocopies. Advance payment is required. Make checks payable to Microfiche Publications. Outside the United States or Canada, postage is $3.00 for a photocopy or $1.00 for a fiche.

Notes

Contribution from the Centre de Spectroscopie Moléculaire de
l'Université de Reims, Laboratoire de Chimie Minérale et
Laboratoire de Chimie Organique Physique,
Faculte des Sciences, Reims, France

Fourier Transform Carbon-13 Nuclear Magnetic Resonance Study of Cyanocuprates(I) in Aqueous Solution

Charles Kappenstein, James Bouquant, and René P. Hugel*

Received July 28, 1978

Our preceding studies on copper(I) cyano complexes, based on X-ray structure determinations and on infrared and Raman spectroscopy, showed a trigonal-planar $\mathrm{Cu(CN)_3}^{2-}$ ion in the solid state[1] and in solution[2] whereas the $\mathrm{Cu(CN)_2}^{-}$ ion was a polymer in the solid state[3] and a mononuclear linear ion in aqueous solution.[2] The vibrational study[2] on the three anions $[\mathrm{Cu(CN)}_n]^{(n-1)-}$, with n = 4, 3, and 2, led to the conclusion that in the copper–carbon bond, the σ-donor character of the cyanide is largely predominant over its π-back-bonding capacity; furthermore a comparison with metal carbonyls shows opposite correlations between CN and CO complexes. In this paper we report a reinvestigation of these results using Fourier transform carbon-13 nuclear magnetic resonance experiments in aqueous solution.

Table I

used compounds	[CN]/[Cu]	predominant species[a] (mol L^{-1})	δ[b]
KCN		CN (2.00)	165.8
NaCN		CN (1.93)	165.8
$K_3Cu(CN)_4$ + KCN	14.60	$Cu(CN)_4$ (0.18) + CN (1.94)	164.7
$K_3Cu(CN)_4$ + KCN	7.93	$Cu(CN)_4$ (0.50) + CN (1.97)	163.9
$K_3Cu(CN)_4$ + KCN	5.91	$Cu(CN)_4$ (1.00) + CN (1.90)	163.1
$K_3Cu(CN)_4$	4.00	$Cu(CN)_4$ (0.97) + $Cu(CN)_3$ (0.05)	161.8
CuCN + KCN	3.70	$Cu(CN)_4$ (0.69) + $Cu(CN)_3$ (0.31)	160.6
CuCN + KCN	3.47	$Cu(CN)_4$ (0.47) + $Cu(CN)_3$ (0.53)	159.5
CuCN + KCN	3.22	$Cu(CN)_4$ (0.22) + $Cu(CN)_3$ (0.78)	157.8
CuCN + KCN	3.01	$Cu(CN)_4$ (0.01) + $Cu(CN)_3$ (1.00)	156.4
CuCN + KCN	2.98	$Cu(CN)_3$ (0.48) + $Cu(CN)_2$ (0.01)	156.0
CuCN + NaCN	2.81	$Cu(CN)_3$ (0.41) + $Cu(CN)_2$ (0.10)	155.1
CuCN + KCN	2.72	$Cu(CN)_3$ (0.36) + $Cu(CN)_2$ (0.14)	154.6
CuCN + KCN	2.70	$Cu(CN)_3$ (0.36) + $Cu(CN)_2$ (0.16)	154.5
CuCN + NaCN	2.60	$Cu(CN)_3$ (0.30) + $Cu(CN)_2$ (0.20)	154.1
CuCN + NaCN	2.48	$Cu(CN)_3$ (0.25) + $Cu(CN)_2$ (0.27)	153.6

[a] The charges are omitted for clarity. [b] ^{13}C Chemical shifts downfield from Me_4Si.

Experimental Section

The ^{13}C NMR spectra were recorded at 26 °C and at 15.1 MHz on a Bruker WP 60 NMR spectrometer. The instrument was locked on D_2O, present in the solution at a 10% concentration.

Aqueous solutions of cyanocuprates(I) were prepared from NaCN or KCN, $K_3Cu(CN)_4$, and CuCN, with CN/Cu ratios covering the range 14.60–2.48 (Table I). The chemical shifts are reported downfield vs. Me_4Si, but were experimentally measured vs. dioxane as internal standard.[4] The CN^- ion is a weak base (the pK_a of HCN is ~9.3) and the chemical shift for HCN was measured in aqueous solution to be 113.1 ppm; thus we have controlled by pH measurements that the concentration of HCN is always very small vs. the one of CN^- ion or the other species present in solution. Moreover the chemical shifts for solutions containing in addition NaOH (10^{-2} mol L^{-1}) showed no discrepancey with the results in Table I.

The knowledge of the successive equilibria[5]

$$CN^- + Cu(CN)_2^- \rightleftarrows Cu(CN)_3^{2-} \qquad (\log K_3 = 5.39)$$

$$CN^- + Cu(CN)_3^{2-} \rightleftarrows Cu(CN)_4^{3-} \qquad (\log K_4 = 2.62)$$

permits us to compute the composition of a whole series of solutions containing different ratios CN/Cu. In contrast with the results of Hirota et al.,[6] only one carbon-13 nuclear magnetic resonance is observed indicating that the complexes are labile and that rapid exchange occurs between coordinated and free cyanide.

The substitution of KCN by NaCN shows no influence and for all the solutions there are one or two predominant species; thus we have three domains, and if we report for each domain the chemical shift vs. the molar fraction in terms of the cyanide content of the complex ions,[7] we obtain three segments (Figure 1). The values of the chemical shifts for the three cyanocuprate ions were calculated through a least-squares method assuming that each segment is a straight line (standard deviations on the last significant digit are given in parentheses): CN^- 165.8 (1) ppm, $Cu(CN)_4^{3-}$ 161.9 (1) ppm, $Cu(CN)_3^{2-}$ 156.2 (1) ppm, $Cu(CN)_2^-$ 149.2 (3) ppm. The value for $Cu(CN)_2^-$ had to be extrapolated because of the low solubility of the dicyanocuprate salts; a broad signal is observed for the lowest δ values in the last domain, which may be due to a diminution of the exchange rates of the cyanide ions.

Results and Discussion

When the coordination number of copper decreases from 4 to 2, the ^{13}C magnetic resonance signal of the cyanide ligand goes upfield, i.e., toward a better shielding (Figure 1).

We observe also a correlation between the chemical shifts and the cyanide symmetric stretching frequencies (Figure 2, left side). This type of correlation is well-known for different metal carbonyl derivatives[8-10] (ν(CO) vs. $\delta(^{13}C)$), but we know only one for cyano compounds; Gansow[11] has reported a study about transition-metal derivatives (Mo, W, Mn, and Fe) of polycyanoolefins. We find here the same trend for copper(I) cyanides as in the previous studies, that means a better shielding of the carbon atom with an increasing CN stretching frequency.

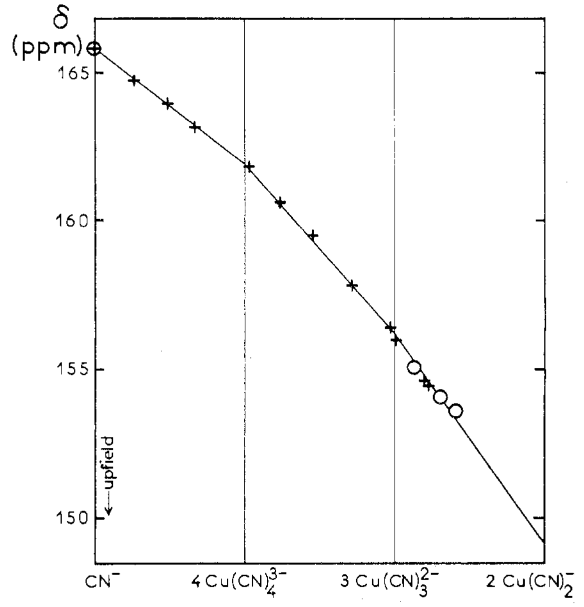

Figure 1. Variation of the ^{13}C chemical shift vs. the composition of the solutions in terms of cyanide content: (+) potassium salts, (○) sodium salts.

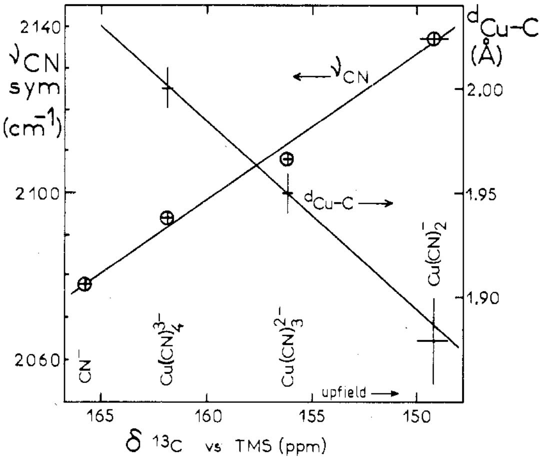

Figure 2. Correlations between chemical shifts and ν(CN) symmetric stretching frequencies (left side) and copper–carbon bond distances (right side).

But when we look toward the metal–carbon bond considering the copper–carbon bond length, we obtain another correlation between chemical shifts and these distances. Bodner[8] has already quoted this correlation for metal carbonyl complexes and found that the chemical shifts go upfield when the metal–carbon bond distances increase. Here it is interesting to note that for cyanocuprates the reverse for this correlation is true (Figure 2, right side and note 12): the chemical shifts go upfield as the copper–carbon bond lengths decrease, that is when the bond becomes stronger.

The meaning of these effects for cyano and carbonyl compounds is difficult to rationalize in terms of σ and π bonding. If we consider also the strong shielding observed when going from CN^- toward HCN (~53 ppm upfield), we can only propose an interpretation in terms of a good bonding between copper and carbon, in the case of cyanides, that is in agreement with our previous vibrational studies.[2] In conclusion we can say that while the first correlation (ν(CN) vs. $\delta(^{13}C)$) gives an analogy between cyano and carbonyl ligands, the second one (d(Cu–C) vs. $\delta(^{13}C)$) shows clearly a difference between these two ligands.

Registry No. KCN, 151-50-8; NaCN, 143-33-9; $K_3Cu(CN)_4$, 14263-73-1; CuCN, 544-92-3; CN^-, 57-12-5; $Cu(CN)_4^{3-}$, 19441-11-3; $Cu(CN)_3^{2-}$, 16593-63-8; $Cu(CN)_2^-$, 18973-62-1.

References and Notes

(1) C. Kappenstein and R. P. Hugel, *Inorg. Chem.*, **17**, 1945 (1978).

(2) C. Kappenstein, R. P. Hugel, A. J. P. Alix, and J. L. Beaudoin, *J. Chim. Phys.*, **75**, 427 (1978).

(3) C. Kappenstein and R. P. Hugel, *Inorg. Chem.*, **16**, 250 (1977).

(4) Originally all chemical shifts were calculated vs. CN^- as standard, that is vs. the resonance frequency of cyanide solution. Later dioxane was used as standard (5%) for three solutions and we have checked the consistency of the results with the first ones. Chemical shift of dioxane vs. Me_4Si is 67.4 ppm.

(5) C. Kappenstein and R. Hugel, *J. Inorg. Nucl. Chem.*, **36**, 1821 (1974); *Rev. Chim. Miner.*, **6**, 1107 (1969).

(6) M. Hirota, Y. Koike, H. Ishizuka, A. Yamasaki, and S. Fujiwara, *Chem. Lett.*, 853 (1973).

(7) That is for example for the first domain: $\delta(\text{ppm}) = \delta(Cu(CN)_4)(x) + \delta(CN)(1 - x)$ with $x = 4[Cu(CN)_4]/([CN] + 4[Cu(CN)_4])$.

(8) G. M. Bodner and L. J. Todd, *Inorg. Chem.*, **13**, 1335 (1974).

(9) G. M. Bodner, *Inorg. Chem.*, **13**, 2563 (1974); **14**, 1932 (1975); **14**, 2694 (1975).

(10) O. A. Gansow, D. A. Schexnayder, and B. Y. Kimura, *J. Am. Chem. Soc.*, **94**, 3406 (1972).

(11) O. A. Gansow, A. R. Burke, R. B. King, and M. S. Saran, *Inorg. Nucl. Chem. Lett.*, **10**, 291 (1974).

(12) The variations are +4 cm^{-1} ppm^{-1} for the first correlation (ν(CN)) and −0.009 Å ppm^{-1} for the second one (d(Cu–C)), to compare to the values taken from Bodner and Todd[8] for different metal carbonyls: +6 to +12 cm^{-1} ppm^{-1} and +0.006 Å ppm^{-1}. The Cu–C bond length for $Cu(CN)_2^-$ is taken as 1.88 ± 0.02 Å.

Contribution from the Department of Chemistry,
Auburn University, Auburn, Alabama 36830

Hydrolysis-Assisted Formation of a Mononuclear, Five-Coordinate Dihydroxotriiodocobaltate(II) Ion

W. L. Darby and L. M. Vallarino*

Received January 26, 1979

Crystalline hydroxo complexes of the transition-metal ions are extremely scarce, and the few known examples usually have dimeric or oligomeric structures in which the OH groups act as bridging ligands.[1] Accordingly, there is an almost complete lack of data regarding the characteristic ligating features of the OH^- anion toward transition-metal ions. In this note, we report the preparation and characterization of a crystalline compound which represents an unusual example of a mononuclear hydroxo complex of a first-row transition-metal ion, as well as a unique five-coordinate Co(II) species containing only simple negative ligands.

Experimental Section

Synthesis of $(LH)_2[Co(OH)_2I_3]I$, Where LH is $(H)(CH_3)N^+(CH_2CH_2)_2N^+(CH_3)_2$. A mixture of the green $[CoI_3L]$ complex[2] (600 mg, 1 mmol) and of the colorless trimethylpiperazinium iodide (260 mg, 1 mmol) was suspended in anhydrous ethanol (10 mL) and heated with stirring until the trimethylpiperazinium iodide was dissolved. The hot stirred suspension was treated with 2 drops (0.4 mL) of water; the green solution thereby turned almost colorless, and some of the green solid dissolved. As the mixture cooled down to room temperature, the suspended solid changed to small dark blue crystals. Additional dark blue crystals separated after 1 mL of triethyl orthoformate was added, with swirling, to the cooled suspension. The crystals were filtered, washed with a small volume of chilled anhydrous ethanol, and dried in vacuo; yield 490 mg (56%).

Deuterated $(LD)_2[Co(OD)_2I_3]I$ was prepared similarly to the hydrogen analogue, by using deuterioethanol as the solvent and deuterium oxide as the reagent. From the infrared spectrum the extent of deuteration was estimated to be 70–80%. Little or no hydrogen–deuterium exchange occurred when the crystalline hydrogen complex was exposed to D_2O vapor or suspended in deuterioethanol containing a small amount of D_2O.

Characterization of $(LH)_2[Co(OH)_2I_3]I$. Anal. Calcd for $C_{14}H_{38}N_4O_2I_4Co$: Co, 6.85; I, 58.96. Found: Co, 6.9; I, 59.2. The compound is paramagnetic, with $\mu_{\text{eff}} = 4.45\ \mu_B$ (measured at room temperature with a Gouy balance by using $Hg[Co(NCS)_4]$ as the standard). The infrared spectrum (4000–180 cm^{-1}) was obtained with a Perkin-Elmer Model 580 spectrophotometer by using Nujol and hexachlorobutadiene mulls between cesium iodide and polyethylene plates. (Polystyrene served as the calibration standard.) Characteristic stretching absorptions (cm^{-1}): ν(OH) 3260–3225 (vs, br), $\nu(N^+H)$ 2600 (vs, vbr), ν(Co–OH) 470 (m), ν(Co–I) 208 (vs). The hydrogen-sensitive stretching modes shifted upon deuteration: ν(OD) 2420, $\nu(N^+D)$ 1900, ν(Co–OD) 460 cm^{-1}. The remaining pattern (1500–180 cm^{-1}) closely resembled that of the trimethylpiperazinium cation in the iodide and perchlorate salts. The diffuse reflectance electronic (d–d) spectrum was obtained with a Cary Model 17 spectrophotometer by using magnesium carbonate as the reference. Observed absorptions (10^3 cm^{-1}): 7.0, 13.6, 16.6 (midpoint of a broad asymmetric band), 22.3 (vw), 24.7 (vw).

Thermal Behavior of $(LH)_2[Co(OH)_2I_3]I$. Crystalline $(LH)_2[Co(OH)_2I_3]I$, when heated to about 120 °C, changed to a heterogeneous mixture of green CoI_3L and colorless L^+I^-, identified from their infrared and electronic spectra. The color change was accompanied by a mass loss, and the thermogram (obtained with a Du Pont Model 950 thermal analyzer in the TGA mode) had a single-step shape. The vapor evolved, collected in a cold trap at −80 °C, was identified as pure water from its NMR spectrum. Mass loss: calcd for 2 H_2O, 4.18%; found, 4.0%. With the Du Pont thermal analyzer in the DTA mode, the sharply endothermic "water-loss reaction" was found to take place within a 5 °C interval, centered at 121 °C for the freshly prepared crystalline compound.

Attempted Preparation of Pure $(LH)_2[Co(OH)_2I_3](ClO_4)$. The green CoI_3L (300 mg, 0.5 mmol) and trimethylpiperazinium perchlorate (115 mg, 0.5 mmol) were suspended in ethanol (7 mL) and the mixture was warmed gently until the white needles of the perchlorate were partly dissolved. A drop of water was added, and within minutes the suspended green solid changed to dark blue, while some of the white crystals changed in appearance. (Under a microscope, long needles as well as platelets were detected.) It was not possible to completely separate the blue from the white crystals owing to their similar solubilities. However, in repeated experiments, the cobalt-to-iodine mole ratio of this mixed product was found to be approximately 1 to 3.5, indicating that substitution of the "ionic" iodide by ClO_4^- had occurred, although not completely. From the infrared spectrum, the white crystals were identified as the starting material, $L^+ClO_4^-$ (needles), mixed with a small amount of the perchlorate of the protonated trimethylpiperazinium (platelets).

Results and Discussion

The monopositive trimethylpiperazinium cation L—a weak base of $pK_a = 4.3$—is known to act as a ligand toward transition-metal ions. Specifically, L coordinates to cobalt(II) halides forming crystalline, zwitterionic complexes of the general formula CoX_3L,[2] which have a pseudotetrahedral geometry with C_{3v} symmetry.[3] While not particularly sensitive to atmospheric moisture, these CoX_3L complexes readily dissolve in water, undergoing complete decomposition. For the iodo complex, however, reaction with a limited amount of water under controlled conditions results in the formation of a new complex, isolated as dark blue crystals of empirical formula $L_2{\cdot}CoI_4{\cdot}2H_2O$.

For assignment of the coordination formula of this new complex, the following experimental evidence is especially relevant.

(1) The infrared spectrum shows no absorption in the 1600–1650 cm^{-1} region, where the deformation vibration of coordinated water commonly appears as a strong band. However, the spectrum shows two major hydrogen-sensitive absorptions in the higher energy region: One absorption appears as a strong band centered at 3240 cm^{-1} (2420 cm^{-1} in the deuterated species), characteristic of the OH stretching of metal hydroxides.[4] The other absorption appears as a very

0020-1669/79/1318-2617$01.00/0