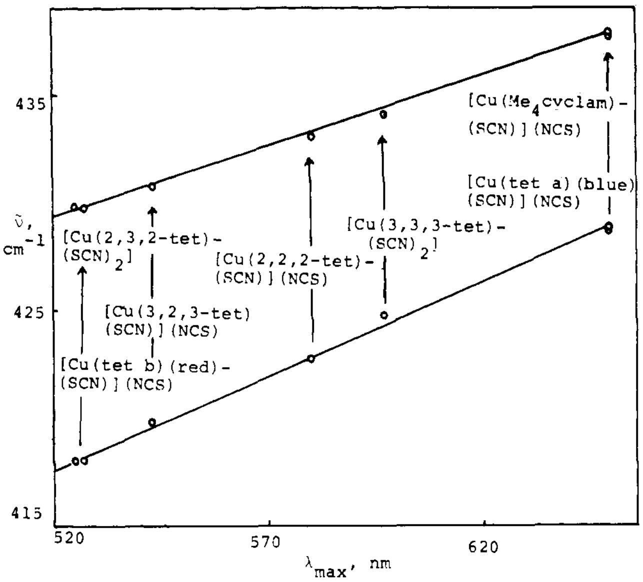
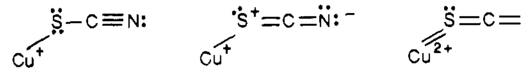


Figure 3. Plot of the N–C–S bending frequencies of CuL$(SCN)_2$ against the electronic absorption maximum for CuL$(ClO_4)_2$.

where L is a tetraamine or a diimine–diamine ligand, in aqueous solution (Table III) is considered an approximate measure of the degree of distortion of the CuN_4 plane.[36,37] As shown in Table III, when the absorption maximum for CuL$(ClO_4)_2$ is larger than 525 nm, the degree of distortion of the CuN_4 plane is large and the thiocyanato group is bonded to Cu(II) through the sulfur atom (M–SCN); when the absorption maximum for CuL$(ClO_4)_2$ is smaller than 525 nm, the degree of distortion of the CuN_4 plane is small and the axial isothiocyanato group is bonded to Cu(II) through the nitrogen atom (M–NCS).

For these S-bonded copper(II) complexes, it is interesting to note that both the C–S stretching frequency and the N–C–S bending frequencies of the axial thiocyanato-*S* group increase as the wavelength of the maximum of the d–d band of the complex increases, i.e. [Cu(tet b)(red)(SCN)](NCS) < [Cu(2,3,2-tet)$(SCN)_2$] < [Cu(3,2,3-tet)(SCN)](NCS) < [Cu(2,2,2-tet)(SCN)](NCS) < [Cu(3,3,3-tet)$(SCN)_2$] < [Cu(Me$_4$cyclam)(SCN)](NCS), [Cu(tet a)(blue)(SCN)](NCS). In general, three resonance structures (I–III) can be written for the thiocyanato-*S* group, with I somewhat more important than each of the other two.



I II III

As the degree of back-bonding of metal nonbonding electrons into vacant antibonding π-orbitals of the thiocyanato-*S* group increases, the contribution of structure III increases; the C–S bond order thus increases, as do the C–S stretching frequency and N–C–S bending frequencies. For the same reasons discussed previously the degree of back-bonding increases as the distortion of the plane of the four amino nitrogen atoms increases. These trends lead us to think that there may be a linear relationship between the C–S stretching frequency of CuL$(SCN)_2$ and the electronic absorption maxima for CuL$(ClO_4)_2$ and a linear relationship between the N–C–S bending frequencies of CuL$(SCN)_2$ and the electronic absorption maxima for CuL$(ClO_4)_2$. These suggested linear relationships are shown in Figures 2 and 3.

Acknowledgment. The support of the Chemistry Research Center, National Science Council of the Republic of China, under Grants NSC 74-0208-M007-08 and NSC 75-0208-M007-04 is gratefully acknowledged. We are grateful to Dr. Chi-Chao Wan and Yuan-Chung Hsieh for performing elemental analyses and for providing laboratory facilities.

Registry No. [Cu(tet b)(blue)(NCS)](SCN), 103530-17-2; [Cu(cyclam)]$(NCS)_2$, 103439-52-7; [Cu(Me$_4$cyclam)(SCN)](NCS), 103439-54-9; [Cu(*N-meso*-trans[14]diene)]$(NCS)_2$, 103439-55-0; [Cu(*N-rac*-trans[14]diene)]$(NCS)_2$, 103439-56-1; [Cu(cis[14]diene)]$(NCS)_2$, 103439-57-2; [Cu(tet a)(blue)(SCN)](NCS), 103530-18-3; [Cu(tet a)(red)$(NCS)_2$], 103439-58-3; [Cu(tet b)(red)(SCN)](NCS), 103530-20-7; [Cu(2,2,2-tet)(SCN)](NCS), 24555-89-3; [Cu(2,3,2-tet)$(SCN)_2$], 103439-59-4; [Cu(3,3,3-tet)$(SCN)_2$], 103439-60-7; [Cu(3,2,3-tet)(SCN)](NCS), 103439-62-9.

Supplementary Material Available: A table showing the analytical data of the thiocyanate and isothiocyanate complexes (1 page). Ordering information is given on any current masthead page.

---

(36) Liang, B.-F.; Chung, C.-S. *Inorg. Chem.* **1980**, *19*, 572–574.
(37) Wu, S.-Y.; Lee, C.-S.; Chung, C.-S. *Inorg. Chem.* **1984**, *23*, 2548–2550.

Contribution from the Department of Chemistry,
Oregon State University, Corvallis, Oregon 97331

Room-Temperature Fused Salts Based on Copper(I) Chloride-1-Methyl-3-ethylimidazolium Chloride Mixtures. 2. Reactions with Dioxygen[1]

Steven A. Bolkan and John T. Yoke*

Received March 11, 1986

As the composition of $n/(1-n)$ CuCl/MeEtImCl melts is varied, the apparent stoichiometry of the reaction with O_2 in the course of several days at 33 °C varies from about 8/1 Cu(I)/O_2 at $n = 0.60$ to 4/1 Cu(I)/O_2 at $n = 0.50$. At a higher temperature, or at $n = 0.40$ at 33 °C, more O_2 is taken up, and in addition to oxidation of copper, formation of 1-methyl-3-ethylimidazolone and water is extensive. The viscous black liquid products show anomalous paramagnetism and catalyze the oxidative polymerization or coupling of 2,6-dimethylphenol. When heated in vacuo, they lose water and the residue is nearly diamagnetic. The organic salt MeEtImCl does not react with O_2. When $CuCl_2$ and CuO are heated with MeEtImCl to 100 °C in vacuo, a black liquid is formed containing 1-methyl-3-ethylimidazolone.

Introduction

Physical properties have been reported[2] for mixtures of copper(I) chloride and 1-methyl-3-ethylimidazolium chloride, $n/(1-n)$ CuCl/MeEtImCl. These mixtures are liquid electrolytes down to about −50 °C over the mole fraction range $0.33 \leq n \leq 0.67$. They may have practical application in batteries. Their electrochemical properties will be described separately.[3] The melts, whose colors vary from pale yellow to light green with increasing n, darken rapidly in air and become paramagnetic as copper(II) is formed.

---

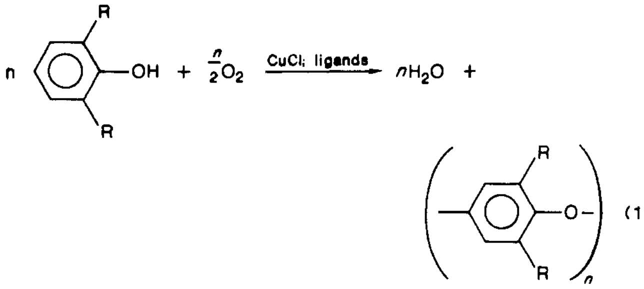
(1) Taken from the Ph.D. Dissertation of S.A.B.; supported in part by a grant from the Oregon State University Research Council.
(2) Bolkan, S. A.; Yoke, J. T. *J. Chem. Eng. Data*, **1986**, *31*, 194.
(3) Bolkan, S. A.; Yoke, J. T., to be submitted for publication.

0020-1669/86/1325-3587$01.50/0

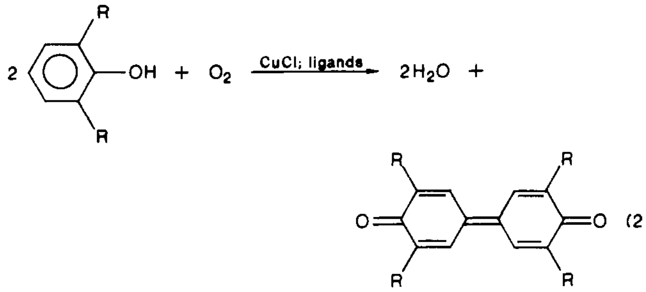
Table I. Reaction of O_2 with $n/(1 - n)$ CuCl/MeEtImCl Mixtures at 33 °C

n	time, days	mol of O_2 taken up/mol of Cu	μ_{eff}/Cu, μ_B
0.60	5	0.125	0.90
0.60	4	0.129	
0.60	1	0.128	0.94
0.50	6	0.250	
0.50	6.7	0.265	1.22
0.50	5.9	0.261	1.27
0.50	0.9	0.253	1.16
0.50	1.7	0.259	
0.40	4	0.694	0.54
0.40	10	0.646	

Autoxidation of copper(I) chloride in the presence of water was studied over a century ago.[4] The reaction in anhydrous systems containing donor solvents or other ligands has been of intense interest in recent years.[5-14] Much of this interest[15-20] is due to the catalytic activity of the reaction products in such reactions as



(1)



(2)

The present work concerns the stoichiometry of dioxygen uptake by $n/(1 - n)$ CuCl/MeEtImCl systems and the nature and properties of the reaction products.

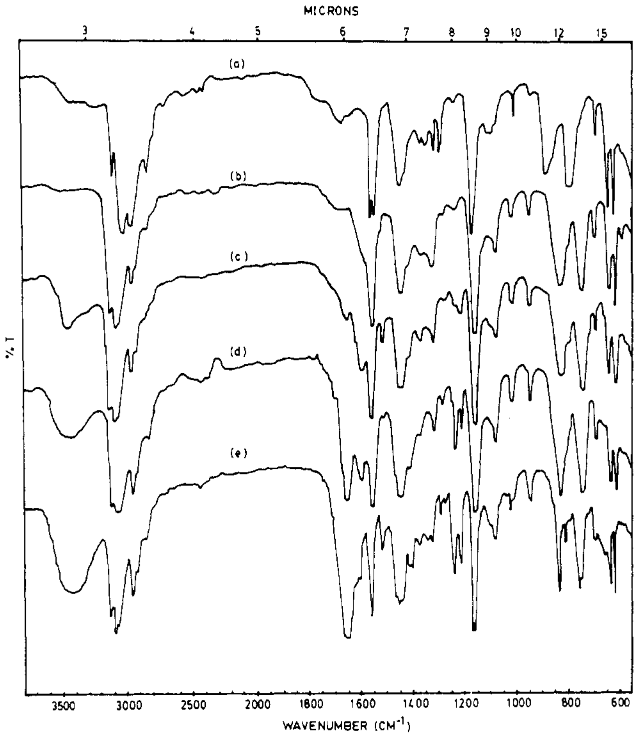


Figure 1. Infrared spectra: (a) MeEtImCl (thin film); (b) 0.50CuCl + 0.50MeEtImCl (neat liquid); (c–e) autoxidation products of nCuCl + $(1 - n)$MeEtImCl (neat liquids), where $n = 0.60$ (c), $n = 0.50$ (d), and $n = 0.40$ (e). The unoxidized fused salts of other compositions studied had spectra identical with spectrum b.

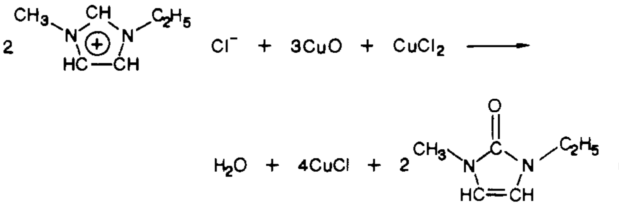
Results and Discussion

Reaction Stoichiometry. When the neat fused salt mixtures in small pressure bottles were exposed to dioxygen gas at about 4 atm pressure and 33 °C, they darkened rapidly and in 1 h or a few hours were black and much more viscous. Rates of dioxygen uptake in different runs cannot be compared. Stirring was not always sufficient to prevent crusts from being formed temporarily, temperature control was only approximate, initial gas pressures were not identical in different runs, and the pressure dropped 10–20% during the reactions. At the reaction times indicated in Table I, the rates of pressure drop had become negligible. The final products were very viscous black liquids.

The apparent stoichiometries, shown in Table I as moles of dioxygen taken up per mole of copper, fall into three groups, corresponding to the compositions of the melts. The reaction

$$4Cu^{+} + O_2 \rightarrow 4Cu^{2+} + 2O^{2-} \qquad (3)$$

would account for 0.250 mol of dioxygen/mol of copper. Autoxidation of melts of composition $n = 0.60$ shows a halt at about half this value. The infrared spectrum (4000–600 cm⁻¹) of the product (Figure 1) is nearly unchanged from that of the starting material at this point. There is no evidence for peroxide formation, although the characteristic peroxide region just above 800 cm⁻¹ is partially obscured by cation absorptions. At the $n = 0.40$ composition, dioxygen consumption is far in excess of that required by eq 3 and new intense C=O, C—N, and O—H bands appear in the infrared spectrum. Water and 1-methyl-3-ethylimidazolone can be isolated from the reaction mixture. One way to represent their formation is by the reaction



(4)

---

(4) Berthelot, M. *Ann. Chim. Phys.* **1880**, *20*, 503.
(5) Finkbeiner, H.; Hay, A. S.; Blanchard, H. S.; Endres, G. F. *J. Org. Chem.* **1966**, *31*, 549.
(6) Kramer, C. E.; Davies, G.; Davies, R. B.; Slaven, R. W. *J. Chem. Soc., Chem. Commun.* **1975**, 606.
(7) Rogic, M. M.; Demmin, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 5472.
(8) Davies, G.; El-Shazly, M. F.; Kozlowski, D. R.; Kremer, C. E.; Rupich, M. W.; Slaven, R. W. *Adv. Chem. Ser.* **1979**, *No. 173*, 178.
(9) Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchinson, J. P.; Rupich, M. W.; Watkins, K. O. *Inorg. Chem.* **1979**, *18*, 2296.
(10) La Pinte, C.; Riviere, H.; Roselli, A. *J. Chem. Soc., Chem. Commun.* **1981**, 1109.
(11) Balogh-Hergovich, E.; Speier, G. *Transition Met. Chem. (Weinheim, Ger.)* **1982**, *7*, 177.
(12) Speier, G. Tyeklar, Z.; Rockenbauer, A. *Inorg. Chim. Acta* **1982**, *66*, L69.
(13) Davies, G.; El-Sayed, M. A. *Inorg. Chem.* **1983**, *22*, 1257.
(14) Hopf, F. R.; Rogic, M. M.; Wolf, J. F. *J. Phys. Chem.* **1983**, *87*, 4681.
(15) Hay, A. S.; Blanchard, H. S.; Endres, G. F.; Eustance, J. W. *J. Am. Chem. Soc.* **1959**, *81*, 633.
(16) Blanchard, H. S.; Finkbeiner, H. L.; Russell, G. A. *J. Polym. Sci.* **1962**, *58*, 469.
(17) Endres, G. F.; Hay, A. S.; Eustance, J. W. *J. Org. Chem.* **1963**, *28*, 1300.
(18) Prabiaud, H.; Kodratoff, Y.; Coudurier, G.; Mathieu, M. V. *Spectrochim. Acta* **1974**, *30*, 1389, 1399.
(19) Churchill, M. R.; Rotella, F. J. *Inorg. Chem.* **1979**, *18*, 853.
(20) Willett, R. D.; Breneman, G. L. *Inorg. Chem.* **1983**, *22*, 326.

The imidazolone was characterized by its mass spectrum (parent ion mass 126), its ^{1}H NMR spectrum (which showed the disappearance of the C-2 proton of the 1-methyl-3-ethylimidazolium ion), and its IR spectrum (which had new peaks at 1660 (C=O), 1240 (CH_3—N), and 1218 cm^{-1} (C_2H_5—N) for the now nonaromatic substituted ring; the latter values provide a particularly good estimate for the amount of imidazolone formation in the autoxidation products, as seen in Figure 1.)

At the $n = 0.50$ composition, dioxygen consumption is only slightly in excess of that required by eq 3 and the C=O, C—N, and O—H infrared absorptions are not nearly so intense as at $n = 0.40$. However, analysis of the product for total copper and for copper(II) shows that about 40% of the copper remains in the copper(I) form, so oxidation of the imidazolium cation is significant. At 70–100 °C, autoxidation is rapid and dioxygen consumption is in excess of that required by eq 3 even at $n = 0.60$. This is also attributed to imidazolium cation oxidation.

Paramagnetism of Reaction Products. The magnetic moments shown in Table I were calculated on a total copper basis and are anomalously low. The values are still low even if for the $n = 0.60$ and $n = 0.50$ cases the calculations take into account that the copper(II) content is, respectively, 50% or 60% of the total copper. This would increase the calculated moments by a factor of 1.4 or 1.3, respectively.

For reaction mixtures containing much 1-methyl-3-ethylimidazolone, the magnetic data indicate another complicating chemical reaction. That compound contains two aliphatic tertiary amine functions, and it is well-known[21,22] that such amine ligands are oxidized by copper(II) to polymeric amines coordinated to diamagnetic copper(I). This would explain the very low apparent paramagnetism of the product at the $n = 0.40$ composition, and new IR peaks at 1520 and 610 cm^{-1} observed in heated autoxidation products.

Moreover, when oxidation products of $n = 0.50$ melts are heated in vacuo, water is volatilized and the magnetic moment per copper in the residue drops from 1.2 to about 0.25 μ_B. The EPR signal at 77 K of the oxidation product becomes very much less intense after the sample has been heated in vacuo. These results are attributed to the formation on heating of additional 1-methyl-3-ethylimidazolone by reaction 4, followed by tertiary amine–copper(II) oxidation–reduction to diamagnetic products.

Oxidation of the 1-Methyl-3-ethylimidazolium Cation. The salt 1-methyl-3-ethylimidazolium chloride does not react with dioxygen at 35 °C and 4.4 atm. pressure, yet the C-2 position in the ring is readily oxidized to the ketone under such conditions in the presence of copper(I) chloride. The same imidazolone was obtained by heating 2 parts of 1-methyl-3-ethylimidazolium chloride with a 3:1 mixture of copper(II) oxide and copper(II) chloride according to the stoichiometry of eq 4; the water generated was isolated in 84% yield. The substituted imidazolium chloride, copper(II) oxide, and copper(II) chloride mixture, when heated, formed a viscous black liquid resembling the autoxidation products of the $n/(1-n)$ CuCl/MeEtImCl fused salts.

A number of clusters have been described[8,11–13,19,27] with four copper(II) ions at the corners of a tetrahedron, with four or six chloride ligands on the face centers or edge centers, and often with four exo ligands on the corners. These may have a μ_4-oxo ligand in the center, μ_2-oxo bridges, or corner oxo-donor atom ligands. One possibility for a component of the $n/(1-n)$ CuCl/MeEtImCl autoxidation product would be such a cluster, partly copper(I) and partly copper(II). Intervalence interactions might account for the black color and anomalous paramagnetism. The results of the autoxidation studies at 33 °C show that oxidation of the organic cation is negligible in an acidic melt, intermediate in a neutral melt, and greatly promoted in a basic melt. Presumably this reflects the effect of excess chloride ions in promoting oxo-cluster formation. The oxo cluster would then react with the organic cation to form the imidazolone.

Oxidation of 2,6-Dimethylphenol. In addition, the $n/(1-n)$-MeEtImCl autoxidation products bring about the oxidative polymerization or coupling of 2,6-dimethylphenol, according to reactions 1 and 2. At $n = 0.40$, where there is an excess of chloride ion, the yellow-white polyphenylene oxide was the major product, while as the mole fraction of copper(I) chloride and the reaction temperature were increased, the major product became the crystalline red quinone. The same result has been reported[17] for catalysis of 2,6-dimethylphenol autoxidation by copper(I) chloride–pyridine mixtures; a high py ligand:Cu(I) ratio favors the C–O-coupled polymeric product, while a low ratio favors the C–C-coupled quinone.

Experimental Section

Materials and Equipment. Preparations of the fused salt components and the inert-atmosphere techniques for their handling have been described.[2] Spectrometric measurements were made with Cary 16 UV-visible, Perkin-Elmer 621 IR; Varian EM 360 NMR, MAT Ch 7 MS, and Varian E9 EPR instruments. Magnetic susceptibilities were measured at room temperature by using a Gouy balance and calibration techniques, which have been described.[28] Dioxygen consumption in reactions was determined by measuring the decrease in pressure at constant volume. The apparatus consisted of a steel tank, a large 100 psi Bourdon gauge, a thick-wall Pyrex reaction vessel with magnetic stirrer, and associated valves and copper tubing to permit evacuation of all parts and filling of the tank with compressed oxygen gas. The assembly was inside an air bath with temperature control to ±2 °C. The gauge was calibrated by using it to measure the vapor pressure of dimethyl ether (Matheson) from −1.9 to +20.5 °C and by comparing the values obtained with the values of Cardoso and Bruno.[29] Measured values of the pressure drop when compressed nitrogen in the tank was allowed to expand into the rest of the evacuated apparatus agreed to ±0.1 psi with values calculated from the volumes of the parts. The estimated error in reading the gauge is ±0.1 psi. In a typical gas uptake experiment, this would introduce a 2% error into the calculation of the moles of dioxygen consumed.

Autoxiation of 0.40/0.60 CuCl/MeEtImCl. In a typical experiment, 2.503 g (1.8 mL) of fused salt of composition 0.400 mole fraction of CuCl, containing 7.848 mmol of copper(I), was placed in a 51.5-mL bottle. This was evacuated and then opened, with magnetic stirring, to dioxygen in a volume of 276.1 mL at 40.4 psig and 33 ± 2 °C. With no reaction, the pressure would drop to 32.0 psig. In fact, when the rate of dioxygen uptake had become negligible the pressure was 26.0 psig, corresponding to a consumption of 5.45 mmol of O_2. The final nominal composition based on copper was 1/1.5/0.694 CuCl/MeEtImCl/O_2, M_r 340.5. At 21.5 °C, the gram susceptibility (mean of three determinations) χ_g was $-(0.319 \pm 0.024) \times 10^{-6}$, the diamagnetic correction (gram susceptibility of 0.40/0.60 CuCl/MeEtImCl, mean of seven determinations) was $-(0.688 \pm 0.025) \times 10^{-6}$, the corrected gram susceptibility χ_g^{cor} was $+0.369 \times 10^{-6}$, and the corrected paramagnetic molar susceptibility χ_M^{cor}/Cu was $+125.6 \times 10^{-6}$ cgsemu, giving a calculated μ_{eff} of 0.544 μ_B. The major source of experimental error was loading the viscous liquid into the Gouy tube. The IR spectrum of the black product had intense bands at 1660 (C=O), 3400 (O—H), and 1240 and 1218 cm^{-1} (C—N), which were not in the spectrum of the starting material.

Autoxidation of 0.50/0.50 CuCl/MeEtImCl. In the same way, in a typical experiment, 5.358 g (3.5 mL) of fused salt of composition 0.500 mole fraction of CuCl, containing 21.89 mmol of copper(I), took up 5.69 mmol of O_2. The final nominal composition was 1/1/0.261 CuCl/MeEtImCl/O_2, M_r 253.9, $\chi_g = +2.070 \times 10^{-6}$, diamagnetic correction -0.581×10^{-6}, $\chi_g^{cor} = +2.651 \times 10^{-6}$, $\chi_M^{cor} = 673.1 \times 10^{-6}$ cgsemu, μ_{eff} 1.27 μ_B. The black liquid had medium-intensity absorptions at 1600 and 3400 cm^{-1} and weak absorptions at 1240 and 1218 cm^{-1}. In a thin film between quartz plates it appeared dark green. It had continuous intense absorption across the visible region with no maximum. The total copper content was determined by heating a weighed sample to fumes with HNO_3 and H_2SO_4 and then diluting, adjusting to pH 6 with $NH_4C_2H_3O_2$ buffer, adding an excess of EDTA, heating to boiling, and back-titrating with $CuSO_4$ to the PAN endpoint. Anal. Calcd for CuCl·MeEtImCl·0.261O_2: Cu, 25.02. Found: 24.73. The copper(II) content was determined by placing a weighed sample into 0.60 M HCl, adding an

---

(21) Weiss, J. F.; Tollin, G.; Yoke, J. T. *Inorg. Chem.* **1964**, *3*, 1344.
(22) Lane, T. A.; Yoke, J. T. *Inorg. Chem.* **1976**, *15*, 484.
(23) Bertrand, J. A.; Kelley, J. A. *J. Am. Chem. Soc.* **1966**, *88*, 4746.
(24) Bertrand, J. A. *Inorg. Chem.* **1967**, *6*, 495.
(25) Bertrand, J. A.; Kelley, J. A. *Inorg. Chem.* **1969**, *8*, 1982.
(26) Kilbourn, T.; Dunitz, J. D. *Inorg. Chim. Acta* **1967**, *1*, 209.
(27) Churchill, M. R.; Davies, G.; El-Sayed, M. A.; Hutchinson, J. P.; Rupich, M. W. *Inorg. Chem.* **1982**, *21*, 995.
(28) Stevens, E. D.; Yoke, J. T. *Inorg. Chim. Acta* **1970**, *4*, 244.
(29) Cardoso, E.; Bruno, A. *J. Chim. Phys.* **1923**, *20*, 347.

excess of KI, and titrating the liberated iodine with $Na_2S_2O_3$ to a starch endpoint. Found: 15.15. The autoxidation product of a similar experiment gave a strong EPR signal at 77 K, with $g_{\perp} = 2.08$, $g_{\parallel} = 2.41$. After the sample had been heated in vacuo for 2 h at 140 °C, the intensity of the EPR signal at 77 K was reduced by a factor of 12. Bulk susceptibility measurements on such heated residues in two experiments led to calculated magnetic moments of 0.19 and 0.31 μ_B, respectively. In one case, the sample lost 3.7 wt % water, which was condensed in a cold trap ($\eta_D{}^{29}$ 1.331, lit. 1.332). The absorption at 3400 cm^{-1} disappeared when the water had been volatilized but new peaks appeared at 1520 and 610 cm^{-1}. In another case, the copper(II) content after heating was found to be 4.5%.

Autoxidation of 0.60Cu/0.40CuCl/MeEtImCl. In the same way, in a typical experiment, 7.241 g (4.3 mL) of fused salt of composition 0.600 mole fraction of CuCl, containing 36.81 mmol of copper(I), took up 4.60 mmol of O_2. The final nominal composition was 1/0.667/0.125 $CuCl/MeEtImCl/O_2$, M_r 200.7, $\chi_g = +1.178 \times 10^{-6}$, diamagnetic correction -0.545×10^{-6}, $\chi_g{}^{cor} = +1.723 \times 10^{-6}$, $\chi_M{}^{cor} = 345.9 \times 10^{-6}$ cgsemu, μ_{eff} 0.90 μ_B. The IR spectrum of the black liquid was virtually identical with that of the starting material, with only a slight absorption at 3400 cm^{-1} and an extremely weak absorption at 1660 cm^{-1}.

1-Methyl-3-ethylimidazolone. The autoxidation product of a 0.40/0.60 CuCl/MeEtImCl melt was placed in a continuous extractor with water and extracted with ether. The extract was evaporated and the residue dried with 4A molecular sieve: ^1H NMR (CD_3CN) δ 1.10 (3 H, t, J = 6 Hz, CH_2CH_3, 3.05 (3 H, s, CH_3), 3.47 (2 H, q, J = 6 Hz, CH_2CH_3), 6.20 (2 H, m, CH=CH); MS, m/e (rel intensity) 127 (10), 126 (90, M^+, calcd. 126), 125 (8), 111 (21), 98 (35), 97 (11), 83 (4.5), 74 (40), 69 (17), 62 (10), 61 (100), 60 (20), 56 (13), 55 (4.1), 45 (17), 44 (49), 43 (85), 42 (36), 41 (8.4); IR (thin film) 3160 (w), 3118 (s, H—C=C), 3095 (sh), 2925 (s), 2450 (w), 1660 (vs, br, C=O), 1460 (vs, br), 1405 (vs), 1375 (m), 1295 (w), 1240 (s, N—CH_3), 1218 (s, N—C_2H_5), 1098 (m), 1042 (m), 1012 (m), 945 (m), 810 (s), 780 (w), 747 (s), 665 (s, br), 600 cm^{-1} (m).

Reaction with 2,6-Dimethylphenol. Approximately 4 g each of various fused salt autoxidation products and of 2,6-dimethylphenol were stirred under nitrogen at various temperatures in the range 32–45 °C for 1 h. The reaction mixture was added to 50 mL of methanol plus 1 mL of concentrated HCl, the solution was cooled in an ice/salt bath, 75 mL of water was added in portions, and the mixture was filtered. The precipitate from reactions using $n = 0.40$ autoxidation products was poly(2,6-dimethylphenylene oxide). Its discoloration due to copper salts could be removed by washing with dilute HCl, to give a yellow-white polymer that darkened on standing in air. Reactions using the $n = 0.60$ autoxidation products at the higher temperatures gave the red crystalline 2,2′,6,6′-tetramethyldiphenoquinone, mp 208 °C (lit.[15-17] 214 °C), while mixtures of polymer and the quinone were obtained under intermediate conditions.

Oxidation of 1-Methyl-3-ethylimidazolium Chloride. When a mixture of 1.38 g (10.2 mmol) of anhydrous copper(II) chloride, 2.45 g (30.8 mmol) of copper(II) oxide, and 3.00 g (20.5 mmol) of MeEtImCl was heated to 110 °C in vacuo, a black liquid was formed. The water evolved over 2 h was condensed in a cold trap; it weighed 0.155 g (8.60 mmol) yield, 84% based on eq 4. The infrared spectrum of the residue showed the characteristic absorptions of 1-methyl-3-ethylimidazolone.

Acknowledgment. We thank Scott Goodman and Gregory Witkop for experimental assistance in the work with 2,6-dimethylphenol.

Registry No. CuCl, 7758-89-6; MeEtImCl, 65039-09-0; O_2, 7782-44-7; H_2O, 7732-18-5; 1-methyl-3-ethylimidazolone, 103816-76-8; 2,6-dimethylphenol, 576-26-1; polyphenylene oxide, 9041-80-9; quinone, 106-51-4.

Contribution from the Laboratoire de Cristallographie aux Rayons X, Université de Genève, CH-1211 Genève 4, Switzerland,
and Materials Science and Technology Division and Intense Pulsed Neutron Source Program,
Argonne National Laboratory, Argonne, Illinois 60439

Structural Studies of the Hydrogen Storage Material Mg_2NiH_4. 2. Monoclinic Low-Temperature Structure

P. Zolliker,[†] K. Yvon,*[†] J. D. Jorgensen,[‡] and F. J. Rotella[§]

Received March 28, 1986

The structure of the low-temperature phase of Mg_2NiD_4 was determined from time-of-flight neutron powder diffraction data collected at 298 K. It has monoclinic symmetry (space group $C2/c$, a = 14.343 (5) Å, b = 6.4038 (10) Å, c = 6.4830 (13) Å, β = 113.52 (4)°, Z = 8) and contains four symmetry-independent D atoms. As expected, the D atoms surround the Ni atoms in a nearly regular tetrahedral configuration (average bond lengths Ni–D = 1.54 Å, average bond angles D–Ni–D = 109.4°). Microtwinning parallel to (011) leads to severe anisotropic broadening of the diffraction peaks.

Introduction

Mg_2NiH_4 has been considered as a promising material for hydrogen storage applications, such as in fuel tanks for hydrogen-powered vehicles.[1] Its structure transforms between 240 and 210 °C from a cubic high-temperature (β') modification into a monoclinic low-temperature (β) modification.[2] As shown in the first paper of this series,[3] and later by other workers,[4-6] the high-temperature structure consists of a CaF_2 type metal atom arrangement in which the D atoms surround the Ni atoms in a disordered configuration. As to the room-temperature structure, conflicting results were reported in the literature (for a review see ref 7). The metal atom substructure as determined from X-ray powder diffraction analysis was described in terms of various models and space groups ($C2/m$,[8] Ia,[9] Cc[10]). Diffraction maxima that could not be interpreted by these models were ascribed to a second low-temperature modification of orthorhombic symmetry.[10] The distribution of the hydrogen atoms was determined by two independent neutron diffraction experiments on the deuteride and found to be ordered in one study[11] and disordered in another.[12] In the former study a model consisting of a square-planar deuterium atom configuration around the Ni atoms was

---

[†] Université de Genève.

[‡] Materials Science and Technology Division, Argonne National Laboratory.

[§] Intense Pulsed Neutron Source Program, Argonne National Laboratory.

(1) Buchner, H. In *Proceedings of the 2nd World Hydroen Energy Conference, Zürich, Switzerland, 1978*; Veziroglu, N., Seifritz, W., Eds.; Pergamon: Elmsford, NY, and Oxford, England, 1978; Vol. 4, p 1749.

(2) Gavra, Z.; Mintz, M. H.; Kimmel, G.; Hadari, Z. *Inorg. Chem.* **1979**, *18*, 3595.

(3) Yvon, K.; Schefer, J.; Stucki,; F. *Inorg. Chem.* **1981**, *20*, 2776. For preliminary results see also: Schefer, J.; Fischer, P.; Hälg, W.; Stucki, F.; Schlapbach, L.; Didisheim, J.-J.; Yvon, K.; Andresen, A. F. *J. Less-Common Met.* **1890**, *74*, 65.

(4) Norēus, D.; Olssen, L. G. *J. Chem. Phys.* **1983**, *78*, 2419.

(5) Soubeyroux, J. L.; Fruchart, D.; Mikou, A.; Pezat, M.; Darriet, B.; Hagenmuller, P. *Mater. Res. Bull.* **1984**, *19*, 969.

(6) Zolliker, P.; Yvon K. *Mater. Res. Bull.* **1986**, *21*, 415.

(7) Yvon, K. *J. Less-Common Met.* **1984**, *103*, 53.

(8) Norēus, D.; Werner, P.-E. *Mater. Res. Bull.* **1981**, *16*, 199.

(9) Ono, S.; Hayakawa, H.; Suzuki, A.; Nomura, K.; Nishimiya, N.; Tabata, T. *J. Less-Common. Met.* **1982**, *88*, 63.

(10) Hayakawa, H.; Ishido, Y.; Nomura, K.; Uruno, H.; Ono, S. *J. Less-Common Met.* **1984**, *103*, 277.

(11) Norēus, D.; Werner, P.-E. *J. Less-Common Met.* **1984**, *97*, 215.

(12) Soubeyroux, J. L.; Fruchart, D.; Mikou, A.; Pezat, M.; Darriet, B. *Mater. Res. Bull.* **1984**, *19*, 1119.

0020-1669/86/1325-3590$01.50/0