reaction at $[H^+] = 0.281$ having the larger value. These qualitative results are in keeping with both reactants being of the same charge and not a reaction between a neutral Mn(VII) species and a protonated Ru(II) ion.

The results of this study demonstrate that the various Ru(II) ions present in acidic perchlorate media are considerably less reactive with Mn(VII) than the corresponding Fe(II) complexes. The observation that the unprotonated Ru(II) ion is considerably less reactive that the monoprotonated Ru(II) ion once again points to the importance of a proton in the activated complex in the conversion of Mn(VII) to Mn(VI) when the E° of the reductant ion is greater than 0.56 V.[2,3,13] Perhaps the proton can more effectively reduce the repulsive charge between the negatively charged MnO_4^- and the smaller Fe(II) ions than the larger Ru(II) ions.

Our results and those of Sutter indicate that the proton needed in the reaction of MnO_4^- with $Ru(CN)_6^{4-}$ and $Fe(CN)_6^{4-}$ is brought into the activated complex by the reductant ion rather than the oxidant. The other MnO_4^-–inorganic reductant ion systems that have been investigated ($Mo(CN)_8^{4-}$, $W(CN)_8^{4-}$, VO^{2+}) show the opposite trend, and the oxidant is the protonated species.

Acknowledgment. The authors thank Mr. Stephen Bialkowski (University of Utah) for his computerization of the experimental $[H^+]$ results.

Registry No. MnO_4^-, 14333-13-2; $Ru(CN)_6^{4-}$, 21029-33-4.

---

(13) F. M. Moore and K. W. Hicks, *Inorg. Chem.*, **14**, 413 (1975).

Contribution from the Department of Physical Chemistry, Technical University of Gdańsk, 80-952 Gdańsk, Poland, and the Institute of Molecular Physics of the Polish Academy of Sciences, 60-179 Poznań, Poland

Solution Equilibria of Copper(II) Chloride in Pyridine and Pyridine–Diluent Mixtures

W. LIBUŚ,* S. K. HOFFMANN, M. KLUCZKOWSKI, and H. TWARDOWSKA

Received April 5, 1979

The concentration-independent visible absorption spectrum and lack of electrical conductance of $CuCl_2$ in pyridine both indicate existence of a single solution complex, $CuCl_2(py)_n$, generally believed to be six-coordinate pseudooctahedral. However, the solubility data for the $CuCl_2{\cdot}2py$ solid compound in pyridine–aprotic diluent mixtures of varying composition can best be rationalized in terms of the equilibrium $CuCl_2(py)_4 \rightleftharpoons CuCl_2(py)_3 + py$. At the same time the diluents exert but a very small effect on the visible absorption band of $CuCl_2$, indicating essential lack of changes in the coordination sphere of copper(II) upon dilution. Exceptional in this respect is chloroform whose additions result in decreasing intensity and a blue shift of the band, consistent with the formation of a centrosymmetrical octahedral complex, except at low pyridine concentrations where the spectral changes become reversed. This effect agrees with the expected stabilization of the octahedral complex by the protic solvent due to its H···π-type interaction with the coordinated pyridine molecules enhancing the d_π-electron back-donation from the central metal atom. At the same time it shows existence of a different, less symmetrical environment of the Cu^{2+} cation in the $CuCl_2$ solutions in pure pyridine or in mixtures thereof with the aprotic diluents. In an apparent contradiction to these inferences are the ESR spectra of frozen solutions showing axial symmetry of the complex as well as interaction of the unpaired electron with four equivalent nitrogen nuclei. An explanation is provided by the observation that decreasing temperature induces changes in the visible spectrum of $CuCl_2$ paralleling those induced by chloroform additions, thus showing a drastic change in structure of the solution complex upon freezing. The following scheme of solution equilibria of $CuCl_2$ is proposed in conclusion: $CuCl_2(py)_3 + py \rightleftharpoons CuCl_2(py)_4\ (C_{2v}) \rightleftharpoons CuCl_2(py)_4\ (D_{4h})$, the C_{2v} complex involving essentially five-coordinate copper(II) and one weakly bound pyridine molecule predominating in pure pyridine at room temperature, while decreasing temperature or chloroform additions to pyridine induce formation of the $CuCl_2(py)_4$ centrosymmetrical complex.

Introduction

The well-known crystalline compound $CuCl_2{\cdot}2py$[1,2] dissolves in pyridine (py) to give a nonconducting solution, whose relatively intense absorption band at 775 nm ($\epsilon_{max} = 140$) is independent of concentration.[3] Additions of a noncoordinating solvent (diluent) like chlorobenzene to pyridine result in a sharp decrease in solubility of $CuCl_2{\cdot}2py$ and but a very small change in intensity of the visible absorption band of the solution. The single solution complex indicated by these facts was believed to be six-coordinate pseudooctahedral.[3] However, after pyridine activities had been determined, the solvent activity coefficient calculated as

$$y^\circ = s^* a_{py}{}^{n-2}/s \qquad (1)$$

where s and s^* denote solubilities of $CuCl_2{\cdot}2py$ in the given mixed solvent and in pure pyridine, respectively, and a_{py} is the activity of pyridine, was found to be a reasonable function of solvent composition under the assumption that $n = 3$.[4,5] Supported by the above-mentioned relatively high intensity of the ligand field band, this result indicated existence of the $CuCl_2(py)_3$ complex in the respective solutions. Following our work, Uruska and Szpakowska applied the same argumentation to show formation of the $CuCl_2(iq)_3$ complex in $CuCl_2$ solutions in isoquinoline–chlorobenzene mixtures.[6] In the latter work the ESR spectra of frozen solutions were also determined, and two local environments of the Cu^{2+} ion involving two and three nitrogen atoms of D_{4h} and C_{4v} effective symmetries, respectively, were inferred from the observed superhyperfine lines due to the interaction of the unpaired electron with the nitrogen nuclei. The ESR spectra of the $CuCl_2$ solutions in pyridine[7] and pyridine–diluent mixtures[8,9]

---

* To whom correspondence should be addressed at the Technical University of Gdańsk.

(1) L. E. Orgel and J. Dunitz, *Nature (London)*, **179**, 462 (1957).
(2) J. Dunitz, *Acta Crystallogr.*, **10**, 307 (1957).
(3) W. Libuś and I. Uruska, *Inorg. Chem.*, **5**, 256 (1966).
(4) H. Berek, M. Kluczkowski, and W. Libuś, *Proc. Int. Conf. Coord. Chem., 13th, 1970*, **2**, 221 (1970).
(5) W. Libuś, M. Kluczkowski, A. Klonkowski, and W. Nierzwicki, *J. Chem. Soc., Faraday Trans. 1*, **72**, 2552 (1976).
(6) I. Uruska and M. Szpakowska, *J. Chem. Soc., Faraday Trans. 1*, **72**, 2545 (1976).
(7) W. Schubel and E. Lutze, *Z. Angew. Phys.*, **17**, 332 (1961).
(8) H. R. Gersmann and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1962).

also were reported. In all these studies the $d_{x^2-y^2}$ ground state of the cupric cation and axial symmetry of the ligand field have been well established. The superhyperfine lines due to the nitrogen atoms were observed on the $g_{\perp}$ positions in the spectra of frozen solutions, but the number of interacting nitrogen nuclei has not always been established definitely.[8] The extra absorption lines appearing in the spectra resulted in some deformations of the superhyperfine splitting patterns. Nonetheless the opinion seems to prevail that the ESR spectra are consistent with the D_{4h} symmetry of the chloro–pyridine complex in solution, corresponding to four coordinated pyridine molecules, in contradiction to our thermodynamic results.

In view of the above apparently contradicting evidence we felt it desirable to perform a more detailed study on the solution equilibria of $CuCl_2$ in pyridine. We suspected that additions of chloroform might induce formation of the octahedral complex if not yet existing in pure pyridine, thus providing further support in favor of our previous interpretation. The expected effect of chloroform additions was inferred from our recent finding that protic solvents exert a stabilizing effect on octahedral pyridine complexes due to the H$\cdots\pi$ interaction with the coordinated pyridine molecules.[10,11]

Experimental Section

Materials. The solid compound $CuCl_2{\cdot}2py$ was obtained by pyridine additions to a hot ethanolic solution of the hydrated cupric chloride, followed by cooling of the solution. The product was purified by repeated crystallizations from ethanol containing a small quantity of pyridine, which was added, dried in air, and stored in a desiccator. It proved to be stable over long time intervals, its stoichiometry being checked by the standard EDTA titrimetric copper determination. Pyridine, toluene, and ethyl acetate were purified by standard methods[12] and finally distilled through a 30-plate column. The boiling points of the collected fractions were as follows: pyridine, 115.5 °C; toluene, 110.5 °C; ethyl acetate, 77 °C. Special care was taken to obtain good-quality chloroform. The commercial product was shaken with concentrated sulfuric acid to remove ethanol, washed with water until neutrality was attained, dried over K_2CO_3, and subsequently distilled through the 30-plate column, the fraction boiling at 61.5 °C being collected.

Procedures. Solubilities were determined by the saturating column method described previously.[13] The visible absorption spectra of the solutions were determined by means of either the Perkin-Elmer Model 323 (the temperature dependences) or the Zeiss VSU 2-P spectrophotometer, both equipped with a thermostated-cell compartment. The X-band ESR spectra were recorded at room and boiling-nitrogen temperatures on a JEOL JES-3BX spectrometer with 100-kHz field modulation. Field calibration was checked by using a DPPH free radical. Stock solutions of $CuCl_2$ in pyridine were prepared and used for spectral determinations. Concentrations of the solutions were calculated by using the densities determined independently. The stock solutions were analyzed for copper by standard EDTA titration. Preparations of the solutions and further manipulations were performed in a drybox.

Results and Discussion

Solubility Isotherms. Figure 1 shows the solubility isotherms of the $CuCl_2{\cdot}2py$ solid compound in mixtures of pyridine with toluene, ethyl acetate, and chloroform at 25 °C. The three diluents were chosen as representatives of inert, weakly basic, and protic solvents, respectively. Qualitatively, the isotherms found for toluene and ethyl acetate are similar to those for the other aprotic diluents studied earlier, viz., benzene, chlorobenzene, and *o*-dichlorobenzene,[3-5] in that a sharp decrease in solubility takes place upon increasing diluent content in the mixed solvent. On the other hand, a rather unusual isotherm is observed for chloroform as diluent. The appearance of a maximum in solubility for this system, while the stoichiometry of the solid phase remains unchanged, indicates formation of a new complex in the liquid phase. This is in accord with the expectation that chloroform might induce formation of the $CuCl_2(py)_4$ centrosymmetrical octahedral complex, if not yet existing in the pure pyridine solutions of $CuCl_2$.

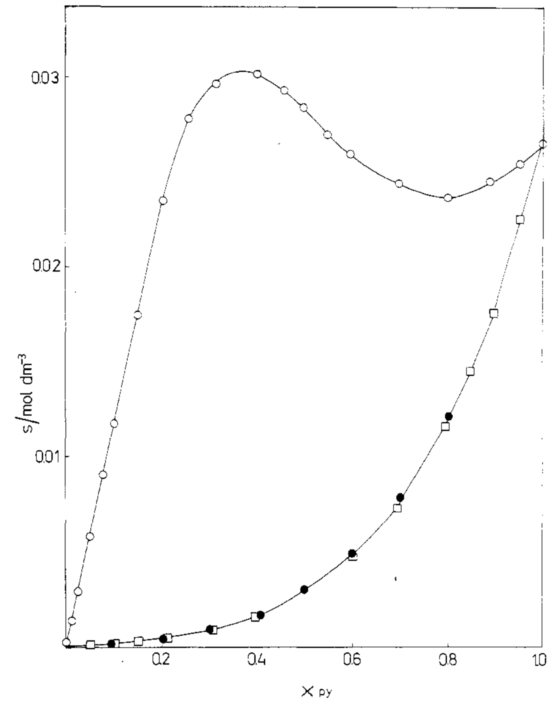

Figure 1. Solubility isotherms of $CuCl_2$ in mixtures of pyridine with toluene (●), ethyl acetate (□), and chloroform (○); 20 °C.

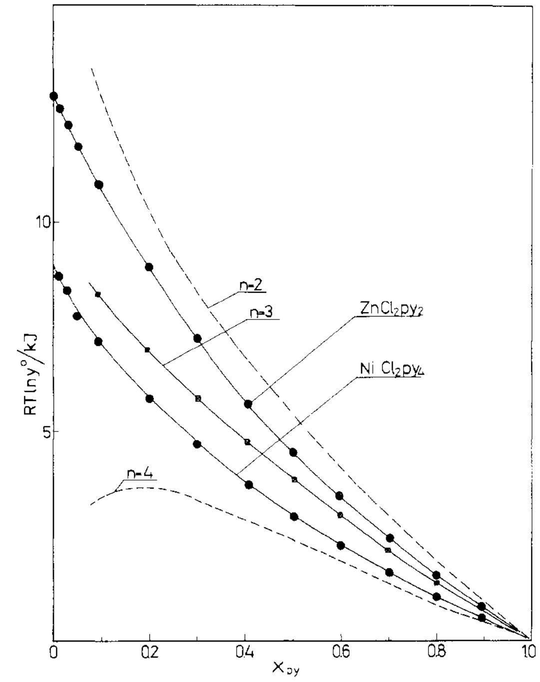

Figure 2. x_{py} dependence of $RT \ln y^{\circ}$, the free energies of transfer of the $NiCl_2(py)_4$ and $ZnCl_2(py)_2$ complexes and of the $CuCl_2(py)_n$ complex, calculated from eq 1 for n = 2, 3, and 4, in mixtures of pyridine with toluene at 20 °C.

---

(9) H. Praliand, Y. Kondrataff, G. Condurier, and M. V. Mathien, *Spectrochim. Acta, Part A*, **30a**, 1389 (1974).

(10) W. Libuš, H. Koniarska, and H. Twardowska, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **27**, 529 (1979).

(11) W. Libuš, K. Chachulska, and M. Mecik, submitted for publication in *Inorg. Chem.*

(12) A. Weissberger, "Organic Solvents", Interscience, New York, 1955.

(13) W. Libuš, M. Kluczkowski, A. Klonkowski, and W. Nierzwicki, *J. Chem. Soc., Faraday Trans. 1*, **70**, 1057 (1974).

(14) W. Libuš and M. Kluczkowski, *J. Chem. Soc., Faraday Trans. 1*, **73**, 1870 (1977).

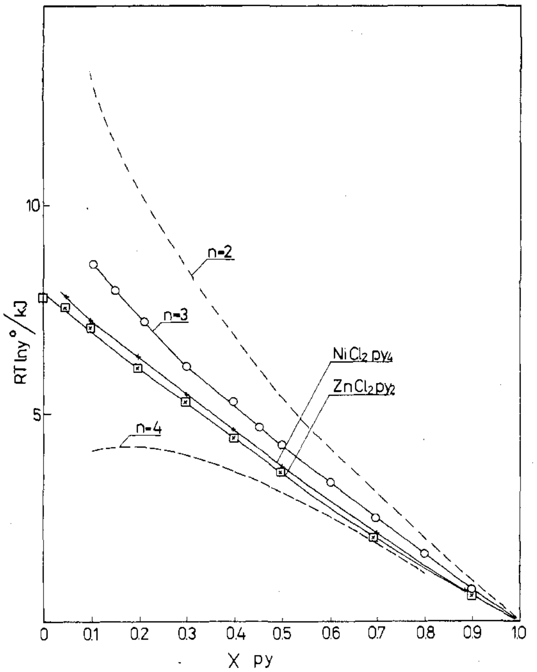

Figure 3. x_{py} dependence of $RT \ln y°$, the free energies of transfer of the $NiCl_2(py)_4$ and $ZnCl_2(py)_2$ complexes and of the $CuCl_2(py)_n$ complex, calculated from eq 1 for $n = 2$, 3, and 4, in mixtures of pyridine with ethyl acetate at 20 °C.

On the assumption that a single solution complex occurs in the saturated solutions of $CuCl_2$ in the pyridine–aprotic diluent mixtures, its solvent activity coefficient may be calculated from the measured solubilities by using eq 1. Activities of pyridine are needed when the stoichiometry of the solution complex is different from that of the solid phase. However, the assumption can safely be made that pyridine activities in the saturated solutions of $CuCl_2$ are essentially the same as those for the respective two-component liquid mixtures.[15] Figures 2 and 3 show plots of $RT \ln y°_n$, the tentatively calculated free energies of transfer of the $CuCl_2(py)_n$ solution complex, for mixtures of pyridine with toluene and ethyl acetate, respectively. Indicated are similar plots for the $NiCl_2(py)_4$ and $ZnCl_2(py)_2$ complexes, the data for the latter being taken from a separate work to be published shortly. We have found earlier that the solvent activity coefficients of the $MX_2(py)_n$-type complexes, where X = Cl or Br and $n = 2$ or 4, to a good approximation are independent of the nature of the central metal atom for systems involving aprotic diluents.[3-5,13-16] Therefore, comparison of the presently calculated plots with those for the above two complexes of the other metals should discriminate between the different possible stoichiometries of the cupric solution complex. Inspection of the figures shows that the stoichiometry of $CuCl_2(py)_2$ certainly is unacceptable, as the free energies of transfer of the complex then derived are markedly higher than those of the $ZnCl_2(py)_2$ reference complex. On the other hand, the free energies of transfer calculated for the $CuCl_2(py)_4$ assumed stoichiometry in both cases approach those for the $NiCl_2(py)_4$ complex as pure pyridine is approached, while they become decreasingly less positive as the pyridine content in the mixed solvent decreases. Corresponding curves pass through flat maxima somewhere at $x_{py} = 0.2$, further decreasing as the pure diluent is approached. We may note that exactly analogous results have been obtained earlier for solutions of $CuCl_2$ in mixtures of pyridine with benzene, chlorobenzene, and *o*-dichlorobenzene.[5] It becomes clear from this behavior that the assumed constant stoichiometry of $CuCl_2(py)_4$ of the solution complex of $CuCl_2$ in the pyridine–aprotic diluent mixtures cannot be true, despite the fact that the visible absorption spectra of the respective solutions remain almost constant (see the next section). The limiting sections of the $RT \ln y°_4$ vs. x_{py} curves coinciding with those of the $NiCl_2(py)_4$ reference complex indicate that a complex of stoichiometry $CuCl_2(py)_4$ predominates in the pure pyridine solutions of $CuCl_2$. However, formation of another complex, involving a lower number of coordinated pyridine molecules, must be assumed to account for further changes in the calculated free energies of transfer as the mole fraction of pyridine decreases. We infer that the new complex is pentacoordinate, $CuCl_2(py)_3$, as the free energies of transfer calculated for this assumed stoichiometry approach values intermediate between those of the $NiCl_2(py)_4$ and $ZnCl_2(py)_2$ reference complexes as the pure diluents are approached (Figures 2 and 3). We should note, at this point, that calculation of the solvent activity coefficient of a given solution complex from the total solubilities is only justified when any other solution complex of the solute is essentially absent. Otherwise, equilibrium concentrations of the complex in the saturated solutions should be used. Alternatively, the latter concentrations could be derived from the measured solubilities, by using a more general relation not considered here,[5,13] if variations in the solvent activity coefficients of the complexes involved with varying solvent composition were known. With neither of the two latter approaches being possible in the present case, we limit ourselves to the conclusion, arising from the above analysis, that a complex of stoichiometry $CuCl_2(py)_4$ prevails in the pure pyridine solutions of $CuCl_2$ at room temperature, while the pentacoordinate complex $CuCl_2(py)_3$ becomes increasingly more important as the activity of pyridine is diminished by diluent addition, in accordance with the equilibrium expression for the reversible reaction

$$CuCl_2(py)_4 \rightleftharpoons CuCl_2(py)_3 + py \qquad (2)$$

However, the $CuCl_2(py)_4$ complex predominating in pyridine must be different from that formed upon chloroform additions, if the effects induced by the latter diluent are to be understood.

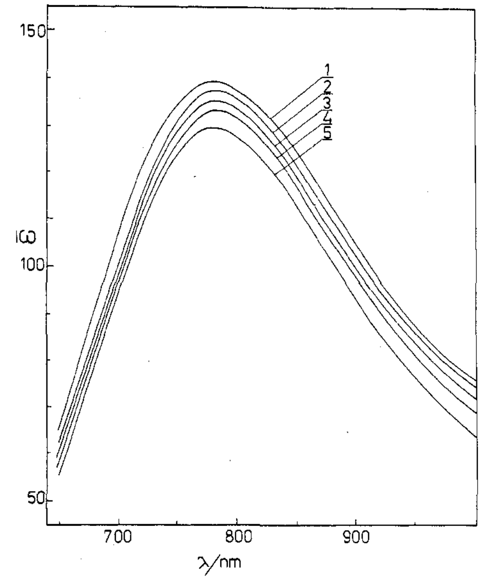

Figure 4. Visible absorption spectra of $CuCl_2$ in pyridine–toluene mixtures (c = 0.005 M) at 20 °C. Mole fractions of pyridine: 1, 1.0; 2, 0.88; 3, 0.80; 4, 0.70; 5, 0.50.

Visible Absorption Spectra. Figures 4 and 5 show the visible absorption spectra of $CuCl_2$ in pyridine–toluene and pyridine–ethyl acetate mixtures, respectively, in each case for a

---

[15] W. Libuš, B. Janaszewski, R. Pastewski, and H. Twardowska, submitted for publication in *J. Solution Chem.*

[16] W. Libuš, A. Klonkowski, and W. Nierzwicki, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **21**, 1057 (1973).

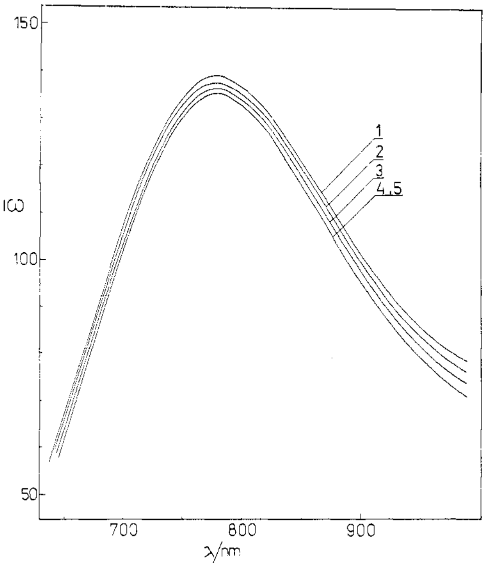

Figure 5. Visible absorption spectra of $CuCl_2$ in pyridine–ethyl acetate mixtures (c = 0.005 M) at 20 °C. Mole fractions of pyridine: 1, 1.0; 2, 0.90; 3, 0.70; 4, 0.49; 5, 0.30.

number of different mixed-solvent compositions. As is seen, in both systems addition of the diluent results in but a small decrease in intensity of the absorption band, without noticeably affecting its position and shape. The observed spectral changes might therefore be interpreted as a "normal" medium effect on the spectrum of a single solution complex. We may note, however, that no changes whatsoever were observed in the spectrum of the $NiCl_2(py)_4$ complex in similar systems.[3,5,16] Therefore, it seems more probable that the small spectral changes now under consideration reflect the changing position of equilibrium 2, while in both complexes involved in the equilibrium the coordination sphere of copper(II) remains essentially the same. This would be the case if coordination of the fourth pyridine molecule consisted in its weak addition to a square-based-pyramidal complex, $CuCl_2(py)_3$, with an out-of-plane copper(II) atom. Recent developments in the field of copper(II) coordination chemistry indicate that this probably is the most preferred stereochemistry of copper(II).[17,24,25] A support for this interpretation seems to be provided by changes in the spectrum of $CuCl_2$ induced by chloroform additions to pyridine. Respective absorption curves are shown in Figures 6 and 7. As is seen, increasing chloroform content up to approximately 0.6 mole fraction brings about a gradual decrease in intensity and a concomitant blue shift of the band originally at 775 nm. Further increase in chloroform content in the mixed solvent results in a reversed effect: the intensity of the band increases and its position is shifted toward lower energies. The limiting spectrum of $CuCl_2$ in almost pure chloroform consists of a band with a maximum at 750 nm and is similar to though not identical with that in pure pyridine. For comparison purposes the latter has also been indicated in Figure 7. It is also worth noting that an isosbestic point is observed in the set of absorption curves shown in the latter figure, indicating a two-species equilibrium of copper(II) within the range of high chloroform contents in the mixed solvent, while the lack of an isosbestic point in Figure 6 indicates the occurrence of more than two solution complexes of copper(II) in the pyridine-rich mixtures.

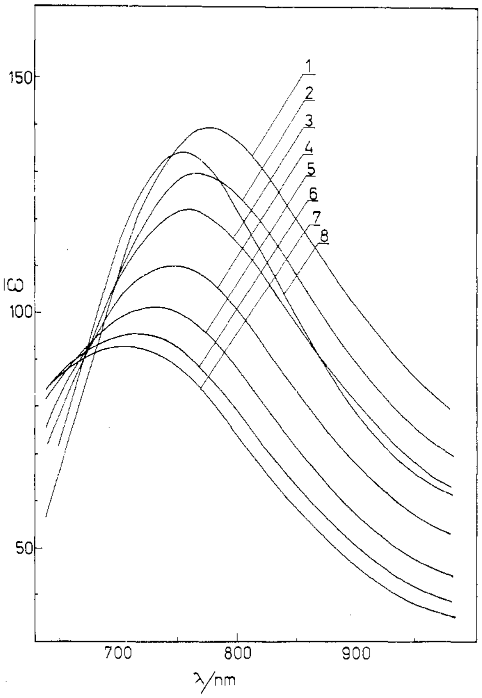

Figure 6. Visible absorption spectra of $CuCl_2$ in pyridine–chloroform mixtures (c = 0.005 M) at 20 °C; $x_{py} > 0.3$. Mole fractions of pyridine: 1, 1.0; 2, 0.89; 3, 0.80; 4, 0.70; 5, 0.60; 6, 0.50; 7, 0.40; 8, 0.011.

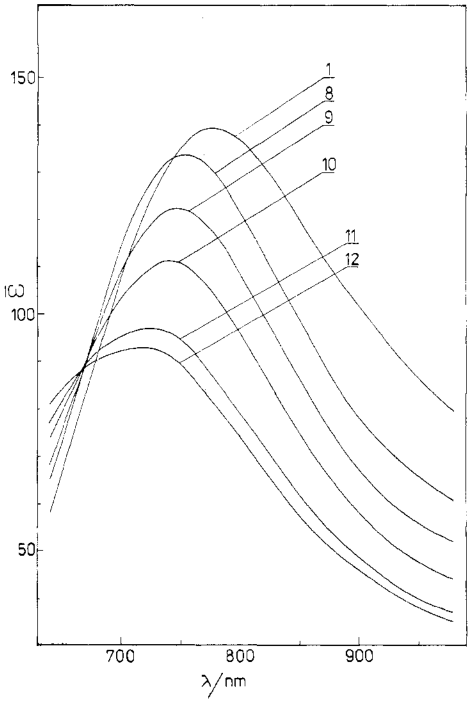

Figure 7. Visible absorption spectra of $CuCl_2$ in pyridine–chloroform mixtures (c = 0.005 M) at 20 °C; $x_{py} < 0.3$. Mole fractions of pyridine: 1, 1.0; 9, 0.050; 10, 0.099; 11, 0.202; 12, 0.258.

It is rather clear that the profound spectral changes induced by chloroform must be due to the changing coordination sphere of copper(II). Neither ionization nor dimerization of the solute comes into play, as the solutions remain nonconducting and their spectra are independent of concentration at any fixed solvent composition. Coordination of chloroform to copper(II) seems to be excluded by virtue of its molecular structure, making it a weak Lewis acid but a very poor Lewis base. It follows that the new complex formed must still be of the $CuCl_2(py)_n$ type, and it seems most probable that chloroform induces formation of the $CuCl_2(py)_4$ octahedral complex with the copper(II) ion occupying the central position, while a

---

(17) M. J. Bew, R. J. Dudley, R. J. Fereday, and B. J. Hathaway, *J. Chem. Soc. A*, 1437 (1971).

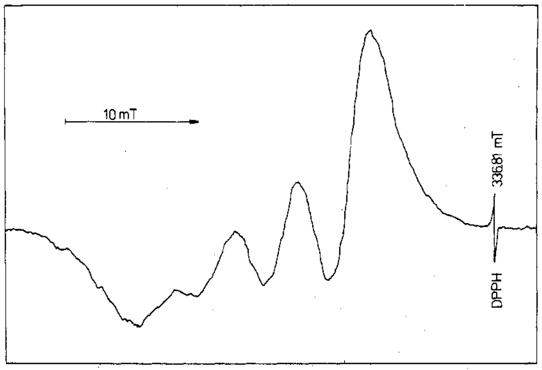

Figure 8. ESR spectrum of $CuCl_2$ in pyridine solution at room temperature (c = 0.022 M).

different one predominates in the $CuCl_2$ solutions in pure pyridine. This is because chloroform is expected to stabilize preferentially those stereochemical arrangements of pyridine molecules around the central metal atom which provide better conditions for the d_π-electron delocalization. It has been well established by Narbutt and Siekierski that chloroform forms hydrogen bonds of the $H\cdots\pi$ type with the related $Co(NCS)_2(\gamma\text{-picoline})_4$ complex,[18,19] and our recent work indicated that the $H\cdots\pi$-type interaction of protic solvents with complexes of the $MCl_2(py)_4$ type is controlled by the d_π-electron delocalization from the central metal atom to the coordinated pyridine molecules.[10,11,15] The latter effect being symmetry dependent should preferentially stabilize certain stereochemistries against others. A striking stabilization of the $CoCl_2(py)_4$ octahedral complex relative to the $CoCl_2(py)_2$ tetrahedral one induced by chloroform additions to pyridine provides a specific example of this general effect.[10,11] Of the $CuCl_2(py)_n$-type complexes having n = 3 or 4, the $CuCl_2(py)_4$ octahedral complex of either D_{4h} or D_{2h} symmetry probably provides the best conditions for the d_π-electron delocalization. Rather obviously, conditions for the d_π–p_π orbital overlap should be much worse for a complex having C_{2v} or C_{4v} symmetry, either six- or five-coordinate with the out-of-plane position of the central metal atom. On the other hand, the trigonal-bipyramidal structure of the $CuCl_2(py)_3$ complex should probably be intermediate between the two extremes, with regard to conditions for the d_π-electron delocalization.[21,24,25]

The marked decrease in intensity of the visible absorption band of $CuCl_2$ brought about by chloroform additions to pyridine (Figure 6) agrees with the supposition that the new complex formed has a centrosymmetrical structure. The concomitant blue shift of the band also is consistent with the six-coordinate complex formed from an essentially pentacoordinate one, as the ligand field strength usually increases with increasing coordination number. We therefore conclude that the $CuCl_2(py)_4$ complex predominating in the pure pyridine solutions of $CuCl_2$, as indicated by the solubility data, is essentially five-coordinate, probably of C_{2v} symmetry, involving one weakly bound pyridine molecule. The latter is readily lost when pyridine activity is decreased, the true pentacoordinate complex of a closely similar structure being formed. However, for chloroform playing the role of the diluent the genuine six-coordinate octahedral complex is formed within the range of intermediate pyridine activities due to the above-mentioned stabilizing effect of the $H\cdots\pi$-type interaction of the complex with the protic diluent. The reversed spectral changes observed within the range of low pyridine concentrations (Figure 7) would then be interpreted as reflecting a new formation of the pentacoordinate complex enforced by decreasing pyridine activity, in accordance with the equilibrium expression for reaction 2. However, the pentacoordinate copper(II) complex formed in the chloroform-rich solutions may likely be involved in some $H\cdots\pi$-type interaction with the protic solvent and thus have a slightly blue-shifted absorption band, as is observed.

Table I. ESR Parameters of $CuCl_2$ in Pyridine-Chloroform Mixtures at 77 K

x_{py}	c/M	$g_\parallel$[a]	$g_\perp$[b]	$-A_\parallel$,[c] 10^{-4} cm^{-1}
1	0.0220	2.275	2.079	173
0.784	0.0172	2.271	2.076	184
0.512	0.0113	2.265	2.074	185
0.252	0.0056	2.252	2.070	187
0.120	0.0027	2.260	2.074	186
0.055	0.0012	2.259	2.072	188
0.020	0.0006	2.257	2.072	188

[a] ±0.005. [b] ±0.002. [c] ±4.

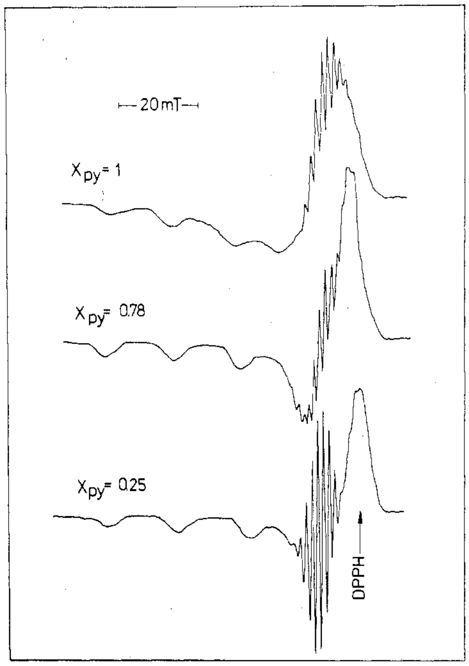

Figure 9. ESR spectra of frozen solutions of $CuCl_2$ in pyridine–chloroform mixtures at 77 K (c = 0.01 M) and at the indicated mole fractions of pyridine.

ESR Spectra. The ESR spectra of $CuCl_2$ in pyridine solution (Figure 8) as well as in pyridine–chloroform mixtures registered at room temperature consist of four hyperfine lines with a characteristic m_I–line-width dependence.[22] The lines are very broad, and the nitrogen superhyperfine structure (shfs) is not resolved. The spectra may be taken as indicating existence of a single copper(II) species in the respective solutions, although the large line widths suggest some dynamic process which may result in structure averaging, precluding detection of species distinguishable in the time scale of the visible spectra. The isotropic g_0 value of 2.125 (±0.007 for x_{py} = 1) remains constant within the experimental error while the composition of the mixed solvent is varied. On the other hand, a_0, the isotropic hfs constant, slightly increases with increasing chloroform content, values of 50, 53, 56, and (57 ± 5) × 10^{-4} cm^{-1} being found at mole fractions of pyridine equal to 1, 0.78, 0.51, and 0.25, respectively. At the same time the lines become

---

(18) J. Narbutt and S. Siekierski, *Rocz. Chem.*, **48**, 1777 (1974).
(19) J. Narbutt, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **22**, 1095 (1974).
(20) J. Narbutt and S. Siekierski, *J. Inorg. Nucl. Chem.*, **38**, 305 (1976).
(21) C. Furlani, *Coord. Chem. Rev.*, **3**, 141 (1968).
(22) H. M. McConnell, *J. Chem. Phys.*, **25**, 709 (1956).

broader as a result of increasing anisotropy of the hfs indicated by increasing $A_\parallel$ (see Table I).

We hoped that direct evidence for the structural transformation of the solution complex of $CuCl_2$ in pyridine–chloroform mixtures of varying composition, inferred from both solubility and visible absorption spectral data, would be obtainable from the ESR spectra of frozen solutions. The results obtained are illustrated in Figure 9 for three solvent compositions at 77 K, while the derived spin-Hamiltonian parameters are listed in Table I. Contrary to the expectation, all the spectra indicate existence of a single copper(II) complex of axial symmetry, as is seen from both the $g_\parallel$ region and the shfs lines, due to the interaction of the unpaired electron with the ^{14}N nuclei of the pyridine ligands, in the $g_\perp$ region. In the pure pyridine solution of $CuCl_2$ the shfs lines are more poorly resolved than in the $x_{py} = 0.25$ solution where the resolution is best and, additionally, the shfs pattern is complicated by the lines of the extra absorption peak from the $m_I = -^3/_2$ hfs line.[23] Inspection of Table I shows that the spin-Hamiltonian parameters derived from the ESR spectra of the frozen solutions vary markedly with varying chloroform content in the mixed solvent. This is reflected in the changing pattern of the perpendicular region of the spectra. The shfs structure of the extra absorption peak loses definition, and the peak shifts upfield as a result of increasing anisotropy of the **A** tensor and decreasing anisotropy of the **g** tensor. For $x_{py} = 0.25$ the extra absorption line is seen as a strong line at the DPPH position (Figure 9). In none of the determined spectra has a resolution of hfs been observed in the $g_\perp$ region. It follows that the latter is smaller than the shfs due to the interaction with the nitrogen nuclei and, as a result, controls the shfs line widths. We may estimate that $A_\perp \leq 4$ cm^{-1} for a solution in pure pyridine and that $A_\perp$ decreases with increasing chloroform content, as indicated by decreasing shfs line widths.

The nine-line shfs pattern of the spectrum with the shfs constant of 15 Gs is characteristic of four equivalent ^{14}N atoms coordinated in a plane with the copper(II) atom, indicating the occurrence of the $CuCl_2(py)_4$ octahedral complex of D_{4h} symmetry in the frozen solutions, in an apparent contradiction to the results discussed in the preceding sections. However, most significant in this connection seems to be the fact that the average values of the g factor $\langle g \rangle = (g_\parallel + 2g_\perp)/3$ derived from the presently considered spectra are markedly different from the isotropic g_0 value of 2.125 found at room temperature. Inspection of Table I shows that $\langle g \rangle > g_0$ for all the solutions studied. This is in accord with the claimed occurrence of an essentially five-coordinate complex in the pyridine solutions at room temperature, as lower g values are expected for a square-based-pyramidal than for an octahedral complex of comparable tetragonal distortion.[17]

Apart from the above question, further considered in the next section, of some interest seem to be changes in the frozen-solution spectra induced by changing the mixed-solvent composition. Decreasing $g_\parallel$ and simultaneously increasing $A_\parallel$ with increasing chloroform content in the mixed solvent (Table I) clearly indicate increasing tetragonal distortion of the complex. Qualitatively, this effect may be accounted for in terms of increasing d_π-electron delocalization from the central metal atom to the coordinated pyridine molecules, induced by the H···π-type interaction of the complex with the protic solvent. However, it would be difficult, at present, to put the discussion on a more quantitative basis, particularly because of the lack of reliable orbital energies.

It is generally believed that the ESR spectra of frozen solutions provide information valid for the solutions at room temperature as well. That this cannot be true for the presently studied solutions of $CuCl_2$ is shown by the temperature effect in their visible absorption spectra discussed in the next section. It follows that the observed change of the ESR spectral parameters upon freezing reflects changing structure of the solution complex. The rather unusual readiness with which this change occurs may in some way be related to the dynamic process, most probably consisting in ligand exchange, responsible for the hfs line broadening observed in the room-temperature spectra. The exchange rate of 7 × 10^7 Hz is estimated from the observed line widths.

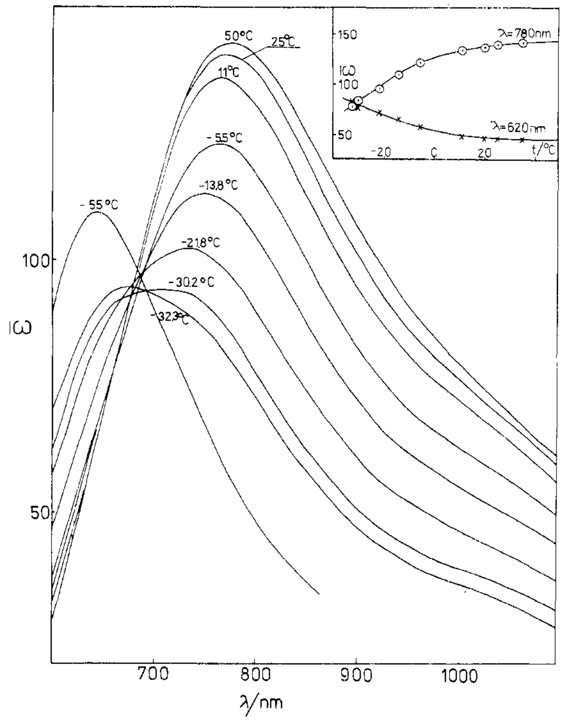

Figure 10. Effect of temperature on the visible absorption spectrum of $CuCl_2$ in pure pyridine (c = 0.005 M).

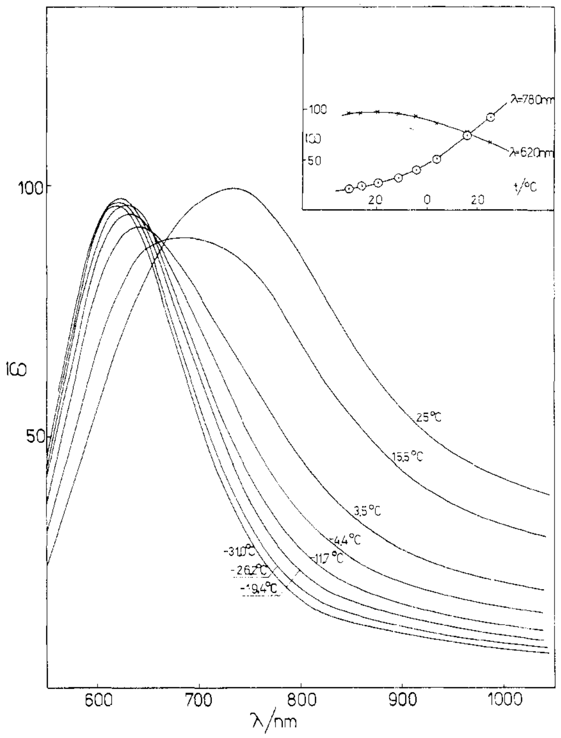

Figure 11. Effect of temperature on the visible absorption spectrum of $CuCl_2$ in pyridine–chloroform mixtures (c = 0.0065 M); x_{py} = 0.266.

---

[23] I. V. Ovchinnikov and V. N. Konstantinov, *J. Magn. Reson.*, **32**, 179 (1978).

Temperature Effect. Figures 10 and 11 illustrate the effect of changing temperature on the visible absorption spectra of $CuCl_2$ for two different solvent compositions: pure pyridine and 0.266 mole fraction of pyridine in the pyridine–chloroform mixture. Inspection of Figure 10 shows that changing temperature has but a small effect on the visible spectrum of $CuCl_2$ in pyridine above some 25 °C. On the other hand, cooling of the solution below room temperature brings about a rapid decrease in intensity of the band originally at 775 nm. The observed concomitant blue shift of the absorption maximum clearly results from superposition of the disappearing band on the new one developing at a higher frequency, as indicated by the isosbestic point at approximately 680 nm. We note that the effect is almost exactly the same as that induced by chloroform additions to the pyridine solution of $CuCl_2$ down to a mole fraction of pyridine equal to ~ 0.25. The development of the new band upon cooling of the solution becomes evident from the effects observed for $CuCl_2$ dissolved in the chloroform–pyridine mixture of $x_{py} = 0.27$ (shown in Figure 11). In this case, the intensity of the lower energy band is considerably reduced already at the starting point at room temperature, and cooling of the solution to -31 °C results in completed development of the higher energy band located at approximately 620 nm, as shown by the mean molar absorption coefficient vs. temperature plots. We recall that further chloroform additions at room temperature resulted in an inversion of spectral changes (Figure 7).

It is clear that the above-described effects are too large to be considered as a normal temperature effect in the spectrum of a single complex. Rather, they indicate changes in the coordination sphere of copper(II) and, qualitatively, are consistent with those expected for the formation of a six-coordinate octahedral complex from an essentially pentacoordinate one predominating at room temperature in pure pyridine. Most significant in this respect seems to be the already mentioned close similarity of the effects induced by decreasing temperature and those resulting from chloroform additions, since the latter are already known to have a strong stabilizing effect on octahedral complexes of the type $MCl_2(py)_4$. It follows that the nature of the complex indicated by the ESR spectra of frozen solutions is consistent with the present inferences but has little in common with the nature of the complex predominating in the pyridine solutions of $CuCl_2$ at room temperature.

Conclusions. Summing up the results of the preceding sections, we propose the following scheme of solution equilibria of copper(II) chloride in pyridine and pyridine–diluent mixtures:

$$\underset{\text{I}}{CuCl_2(py)_3} + py \rightleftharpoons \underset{\text{II}}{CuCl_2(py)_4}\ (C_{2v}) \rightleftharpoons \underset{\text{III}}{CuCl_2(py)_4}\ (D_{4h})$$

The formally six-coordinate complex II predominating in pure pyridine, as indicated by the free energy of transfer results, involves one weakly bound pyridine molecule readily lost upon decreasing pyridine activity to give the pentacoordinate complex I. Very similar visible absorption spectra of complexes I and II indicate that copper(II) is essentially pentacoordinate in both, a "semicoordination" of one pyridine molecule occurring in the latter. Decreasing temperature or chloroform additions to pyridine induce formation of the genuine six-coordinate complex III exhibiting a less intense and blue-shifted visible absorption band. Only the six-coordinate complex involving four equivalent pyridine molecules is detected by the ESR spectra of frozen (77 K) solutions of $CuCl_2$ in pyridine and pyridine–chloroform mixtures, while the room-temperature ESR spectra indicate some dynamic structure averaging.

It seems that the equilibrium coexistence of forms II and III of the formally six-coordinate complex $CuCl_2(py)_4$ may be traced back to a single model characterized by the existence of three minima in the potential energy function of the copper(II) ion along either NCuN axis. Position of the copper(II) ion in the deepest central minimum to give form III of the complex is preferred at low temperatures, while occupation of any of the side minima to give the out-of-plane form II of the complex is induced by increasing temperature. This is because complex II is expected to have a higher entropy than III due to the probability factor of $R \ln 4 = 11.53$ J/(K mol) arising from four equivalent positions of the cupric ion. The model also implies the possibility of a dynamic structure averaging of form II to give an axial complex in the time scale of the ESR spectra through either pseudorotation or ligand exchange. The frequency of 7×10^7 s^{-1} estimated from the hfs line widths of the room-temperature ESR spectra indicates ligand exchange as the structure-averaging mechanism, as it falls within the range of ligand-exchange frequencies encountered for cupric complexes.

The above-proposed model is consistent with the known stereochemical properties of copper(II). Recent developments in this field indicate that the square-based-pyramidal structure of five-coordinate complexes is one of the preferred stereochemistries of copper(II).[17,24,25] It usually involves an out-of-plane location of the cupric ion and sometimes also a weakly bound sixth ligand on the other side of the basal plane. As suggested by Hathaway, this latter situation indicates an asymmetrical charge distribution of the electron pair occupying the d_{z^2} orbital.[24,25] Even better known is the tetragonally distorted centrosymmetrical octahedral structure of copper(II) complexes. Although these and other possible stereochemistries of copper(II) are known to be separated frequently by only small energy differences, resulting in what is referred to as "plasticity" of the coordination sphere of copper(II),[26] only one is embodied at a time in a given crystalline compound, with the rare exception of the occurrence of the "dynamic" Jahn–Teller effect. It seems that absence of the lattice-packing requirements as a structure-determining factor in the liquid state provides favorable conditions for a simultaneous manifestation of the wealth of stereochemistries characteristic of copper(II). Such seems to be the case in the presently studied solutions.

An important factor discriminating between structures II and III of the $CuCl_2(py)_4$ complex is its outer-sphere $H\cdots\pi$-type interaction with protic solvents. As an interaction of this type is controlled by the d_π-electron delocalization from the central metal atom to the π^* orbitals of the coordinated pyridine molecules, it favors the central position of the copper(II) ion for which symmetry conditions for the delocalization are the best. We may note in this connection that increasing chloroform content in the mixed solvent results in increasing energy of the visible absorption band of the centrosymmetrical complex III from 1.56 μm^{-1} in pure pyridine to 1.58 μm^{-1} at $x_{py} = 0.70$ and 1.61 μm^{-1} at $x_{py} = 0.27$, as shown by the low-temperature solution spectra. As the d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$, and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions are responsible for the band and the d_{xz}, d_{yz}, and d_{xy} electron pairs of the central metal atom are potentially available for the delocalization, the latter observation indicates that the outer-sphere interaction with chloroform enhances the d_π-electron delocalization. It follows that the two effects, viz., the d_π-electron delocalization within the complex and the $H\cdots\pi$-type interaction of the complex with the protic solvent, are cooperative, mutually enhancing each other. The question might be raised at this point as to the possible conformations of the complex preferred due to the

---

[24] B. J. Hathaway and A. A. G. Tomlinson, *Coord. Chem. Rev.*, **5**, 1 (1970).

[25] B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).

[26] J. Gažo, I. B. Bersuker, J. Garaj, M. Kabešova, J. Kohout, H. Langfelderova, M. Melnik, M. Serator, and F. Valach, *Coord. Chem. Rev.*, **19**, 253 (1976).

above effects. As several conformations of different symmetries would permit d_π-electron delocalization, the D_{4h} symmetry of the solution complex indicated by the ESR spectra should be considered as an approximation of a more complex situation, at least at room temperature. We postpone a discussion of this question until a further more detailed study has been made.

Registry No. $CuCl_2$, 7447-39-4; $NiCl_2(py)_4$, 36829-43-3; $ZnCl_2(py)_2$, 6843-20-5; $CuCl_2(py)_2$, 6831-72-7; $CuCl_2(py)_3$, 73090-54-7; $CuCl_2(py)_4$, 73136-38-6.

Contribution from the Istituto Chimica Generale e Inorganica,
Università di Firenze, Laboratorio CNR, Florence, 50132 Italy

Nature of the Phase Transitions in $[(C_2H_5)_4N]_2MCl_4$ Complexes (M = Co, Cu)

A. BENCINI, C. BENELLI, and D. GATTESCHI*

Received May 18, 1979

Single-crystal ESR spectra of undiluted $[(C_2H_5)_4N]_2MCl_4$ (M = Co, Cu) are reported. The spectra of the cobalt complex are quite similar to those of the zinc-doped complex. The spectra of the copper complex are temperature dependent, giving $g_\parallel = 2.29$ and $g_\perp = 2.16$ at room temperature, $g_\parallel = 2.10$ and $g_\perp = 2.29$ at intermediate temperature, and $g_\parallel = 2.46$ and $g_\perp = 2.10$ at 4.2 K. This behavior is interpreted as due to dynamic distortions of the pseudotetrahedral chromophores between two equivalent compressions. A similar behavior is suggested also for the cobalt complex.

Introduction

Transition-metal chloride complexes have attracted much interest as simple models to test theories for the interpretation of the electronic properties.[1-7] It has been found, however, that these simple compounds may have an extremely complicated behavior. Indeed they can exhibit a large variety of stoichiometries and structures, which result in a large variability in the observed spectral and magnetic properties of the complexes.[1,8]

Copper tetrachlorides are now well-known to show thermochromism as a consequence either of phase transitions or of gradual changes in the bond angles and lengths.[9] In the case of $(Et_4N)_2MCl_4$ complexes, phase transitions have been observed and studied also for some other metal ions[10-12] (M = Mn, Fe, Co, Ni, Cu, Zn). In particular it was reported that $(Et_4N)_2NiCl_4$ has a tetragonal structure at room temperature, the Co, Mn, and Zn derivatives being isomorphous.[13] ESR spectra of the cobalt-doped zinc complex have shown that the principal axes of the **g** tensor in the low-temperature phase are disordered, showing the presence of eight magnetically nonequivalent sites.[14] The low-temperature g_z axis is found close to the ⟨110⟩ direction of the room-temperature phase, showing that some rearrangements must have taken place in the chromophores. Similar results were obtained for the pure cobalt compound from magnetic susceptibility data[15] although the g values were found to be slightly different. Also the magnetic anisotropy data of the nickel complexes[16] showed abrupt changes indicative of large variations occurring in the crystal structure.

Since ESR spectra of cobalt can be recorded only at low temperature, below the phase transition, it was not possible to follow the dynamics of the phase transition. We have now recorded the ESR spectra of the similar, but not isomorphous, $(Et_4N)_2CuCl_4$ complex and wish to report here the relative results, together with new ESR data on the magnetically undiluted $(Et_4N)_2CoCl_4$, in order to give a more complete model of the nature of the phase transitions in this class of compounds.

Experimental Section

The $(Et_4N)_2CoCl_4$ and $(Et_4N)_2CuCl_4$ complexes were prepared according to the methods reported in the literature.[17]

The crystals of the copper derivative were grown by slow evaporation of concentrated solutions in water or ethanol. From both solvents, yellow crystals of poor quality are deposited, for the most part, in square-tabular form. Single-crystal diffractometer measurements, collected with a Phillips PW 1100 apparatus, using Mo Kα radiation, revealed a tetragonal cell with $a = b = 14.32$ (3) and $c = 12.70$ (2) Å. With these values the most highly developed faces were recognized to be (001). No attempts were done to determine the space group since there is evidence of large disorder in the cell.

For both compounds, the crystals were oriented on a Perspex rod for ESR measurements, according to the extinction properties of polarized light.

ESR measurements down to liquid-helium temperature were performed with the apparatus described previously.[18]

Results

Single-Crystal ESR Spectra of Pure $(Et_4N)_2CoCl_4$. The ESR spectra of single crystals of pure $(Et_4N)_2CoCl_4$, recorded at 4.2 K, were found to be qualitatively in agreement with those of the zinc-doped complex.[14] In particular several signals were observed for a particular orientation of the crystal in the static magnetic field. The lines are broad ($\Delta H_{pp} \simeq 400$ G) so that large overlap of the line occurs, preventing an accurate determination of the g values. The lowest g value, $g = 2.40$, is observed in the (001) plane, quite close to the ⟨110⟩ direction. Contrary to the value used for the calculation of the susceptibility, this value is quite close to that observed in the

---

(1) Smith, D. N. *Coord. Chem. Rev.* **1976**, *21*, 93.
(2) Hatfield, W. E.; Whyman, R. *Transition Met. Chem.* **1969**, *5*, 141.
(3) Caputo, R. E.; Willet, R. D. *Phys. Rev. B* **1976**, *13*, 3956.
(4) Brown, D. B.; Hall, J. W.; Scott, M. F.; Hatfield, W. E. *Inorg. Chem.* **1977**, *16*, 1813.
(5) Gerloch, M.; Lewis, J.; Rickards, R. *J. Chem. Soc., Dalton Trans.* **1972**, 980.
(6) Cohen, E.; Sturge, M. D. *Solid State Commun.* **1977**, *24*, 51.
(7) Putnick, C. F.; Cole, G. M.; Garrett, B. B.; Holt, S. L. *Inorg. Chem.* **1976**, *15*, 826.
(8) Ackermann, J. F.; Cole, G. M.; Holt, S. L. *Inorg. Chim. Acta* **1974**, *8*, 323.
(9) Willet, R. D.; Hangen, J. A.; Lesback, J.; Morrey, J. *Inorg. Chem.* **1974**, *13*, 2510.
(10) Melia, T. P.; Merrifield, R. *J. Chem. Soc. A* **1970**, 1166.
(11) Melia, T. P.; Merrifield, R. *J. Inorg. Nucl. Chem.* **1970**, *32*, 1873.
(12) Melia, T. P.; Merrifield, R. *J. Chem. Soc. A* **1971**, 1258.
(13) Stucky, G. D.; Folkers, J. B.; Kistenmacher, T. J. *Acta Crystallogr.* **1967**, *23*, 1064.
(14) Shankle, G. E.; McElearney, J. N.; Schwartz, R. W.; Kampf, A. R.; Carlin, R. L. *J. Chem. Phys.* **1972**, *56*, 3750.
(15) McElearney, J. N.; Shanker, G. E.; Schwartz, R. W.; Carlin, R. L. *J. Chem. Phys.* **1972**, *56*, 3755.
(16) Gerloch, M.; Slade, R. C. *J. Chem. Soc. A* **1969**, 1022.
(17) Gill, N. S.; Taylor, F. B. *Inorg. Synth.* **1967**, *9*, 136.
(18) Bencini, A.; Gatteschi, D. *Inorg. Chem.* **1977**, *16*, 2141.