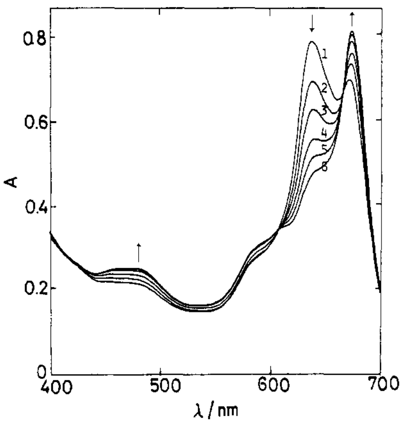

Figure 1. Spectral changes during the oxidation of PcNdPcH in the acetonitrile solution containing 60% (v/v) dichloromethane with irradiation light of λ >320 nm ($[\mathrm{PcNdPcH}]_0 = 1.00 \times 10^{-5}$ mol dm^{-3}): (1) 20 s, (2) 5 min 30 s, (3) 17 min, (4) 25 min, (5) 40 min, and (6) 60 min after irradiation.

Table I. Relative Quantum Yields for Radical Formations under Photoirradiation in the Solvent Mixture of Dichloromethane and Acetonitrile

run	conditions	quantum yield
	$[\mathrm{PcNdPcH}]_0 = 1.00 \times 10^{-5}$ mol dm^{-3}	
1	40% (v/v) CH_2Cl_2	0.51
2	60% (v/v) CH_2Cl_2	0.70
3	70% (v/v) CH_2Cl_2	0.90
4	80% (v/v) CH_2Cl_2	1.00
	$[CH_2Cl_2]_0 = 6.27$ mol dm^{-3}	
5[a]	PcNdPcH	0.64
6[a]	PcYPcH	0.81
7[a]	PcLuPcH	1.00

[a] $[\mathrm{complex}]_0 = 1.00 \times 10^{-5}$ mol dm^{-3}.

source). Electronic spectra were recorded on a Hitachi 124 spectrophotometer. The ESR spectra (X-band) were measured at room temperature with a JEOL-1X spectrophotometer.

Results and Discussion

The solvent mixture of dichloromethane and acetonitrile containing the PcNdPcH complex was irradiated with a wavelength >320 nm (Figure 1). Upon irradiation, absorption bands at 334 and 636 nm of PcNdPcH were shifted to 320 and 676 nm, respectively, with the appearance of a new band around 470 nm characteristic of radical phthalocyanine;[8,9] isosbestic points were found at 330, 357, 600, and 665 nm. The final spectrum was identical with that of the radical PcNd$\dot{\mathrm{P}}$c species.[7,8] The radical was also confirmed by an ESR measurement; the solution after irradiation showed an intense ESR signal at $g = 2.00$, which is typical of a radical species of phthalocyanine.[5,6,9]

Without dichloromethane, the radical was not generated under photoirradiation. Relative quantum yields in the presence of various concentrations of dichloromethane are shown in Table I.[10] The relative quantum yield straightly increases with an increase of the concentration of dichloromethane. The lanthanum(III) complex decomposed under irradiation with light of λ > 320 nm. It is improbable that dichloromethane is excited with a light of λ > 320 nm, and hence the PcLnPcH complex absorbs light energy at first and might form an exciplex with dichloromethane. The excited electron is then transferred to dichloromethane, resulting in radicals:

$$\mathrm{PcLnPcH} + CH_2Cl_2 \xrightarrow{h\nu} (\mathrm{PcLn\dot{P}cH})^+ + \dot{C}H_2Cl + Cl^-$$

$$(\mathrm{PcLn\dot{P}cH})^+ \rightarrow \mathrm{PcLn\dot{P}c} + H^+$$

The similar photooxidations of ruthenocene, a carbonyl(η^5-cyclopentadienyl)iron(I) tetramer, and metal porphyrins in the presence of halocarbons have been reported.[11-13]

The relative quantum yield increases with decreasing ionic radius of the lanthanoid(III) ion (Table I). Since the bond length between the lanthanoid(III) ion and the nitrogen atoms in the macrocycles is shortened with the decrease of the ionic radius, the π–π interaction of the two ring systems must become stronger in the order of the neodymium(III), yttrium(III), and lutetium(III) complexes. This might raise an energy level of the HOMO orbital of the rings, and thus the oxidation of the complex becomes easier in this order.

Acknowledgment. We gratefully acknowledge Dr. Yasuo Kubo for useful discussions and also Professor Yasuo Yamamoto, Shimane University, for his encouragement. This work was supported by a Grant-in-Aid for Scientific Research (No. 60540393) from the Ministry of Education, Science and Culture.

Registry No. PcLaPcH, 11060-90-5; PcNdPcH, 12369-76-5; PcLuPcH, 12369-74-3; PcYPcH, 37239-59-1; PcNd$\dot{\mathrm{P}}$c, 76723-41-6; acetonitrile, 75-05-8; dichloromethane, 75-09-2.

---

(8) Chang, A. T.; Marchon, J. *Inorg. Chim. Acta* **1981**, *53*, L241.

(9) Sugimoto, H.; Higashi, T.; Mori, M. *Chem. Lett.* **1982**, 801. Sugimoto, H.; Higashi, T.; Maeda, T.; Mori, M.; Masuda, H.; Taga, T. *J. Chem. Soc., Chem. Commun.* **1983**, 1234.

(10) The yield of the radical after 3 min of irradiation was obtained by measuring the absorbance decrease at 636 nm (Q-band of the starting complex). The relative quantum yield is estimated as a relative value to the largest one in a series of concentration effects of dichloromethane. The relative quantum yield for the ionic radius effect is also estimated in a similar manner.

(11) Borrell, P.; Henderson, E. *J. Chem. Soc., Dalton Trans.* **1975**, 432.

(12) Bock, A.; Wrighton, M. S. *Inorg. Chem.* **1977**, *16*, 1309.

(13) Gasyna, Z.; Browett, W. R.; Stillman, M. J. *Inorg. Chem.* **1984**, *23*, 382.

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Weak Chloro Complex Formation by Copper(II) in Aqueous Chloride Solutions

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Ramette and Fan[1] have recently criticized our recalculation[2] of spectra and stability constants based on the very reliable spectrophotometric measurements on the copper(II) chloride system made by Schwing-Weill and Khan.[3,4] Ramette and Fan[1] have failed to acknowledge a previous detailed study[5] of copper(II) complex formation in aqueous chloride solution that also forms the basis for our recalculation of Schwing-Weill's data. This is probably the reason for their unjustified criticism and makes it necessary for us to reiterate once more the problems involved.

The reason for our recalculation from the data of Schwing-Weill and Khan was the suspiciously low value for the molar extinction coefficient of the tetrachloro complex at 400 nm ($\epsilon_4 = 216$) compared to that of $CuCl_2$ dissolved in a saturated $CaCl_2$ solution, which has the limiting absorbance $\epsilon^\circ = 950$ at 400 nm. The copper(II) chloride spectra in the UV and in the blue visible region are due to electron-transfer transitions, and as such they are more influenced by the medium than is the case with ligand field spectra.[6] However, there can be no doubt that the limiting molar

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absorbance in concentrated chloride solutions with $[Cl^-] \gtrsim 10$–12 M is that for the tetrachloro complex.[5] The values found for the molar absorbance in 6.2 M $CaCl_2$ at 400 and 436 nm ($\epsilon^\circ = 950$ and 300, respectively) are about 40% lower than the corresponding values in concentrated HCl, LiCl, and $MgCl_2$. It is therefore quite possible that the molar absorbance in 5 M $NaClO_4$ at 400 nm is as low as ~800, but even then this generously low value is nearly 4 times larger than the value ($\epsilon_4 = 216$) calculated by Schwing-Weill and Khan at the same wavelength.

Ramette and Fan[1] are of the opinion that the formation of $CuCl_4^{2-}$ is not complete in 12.4 M $CaCl_2$. This is a misunderstanding since the effective chloride activity is unusually high in saturated $CaCl_2$. We have previously shown[7,8] that the effective chloride activity in strong chloride solutions can be satisfactorily approximated by

$$a_{Cl^-} = [Cl^-]10^{B[Cl^-]-0.5}$$

where B is estimated by Bjerrum[5] for the $CuCl_2$ system to have the value 0.21 in strong $CaCl_2$ solutions. This gives $a_{Cl^-} = 1570$, and applying our value for the fourth consecutive constant $K_4 = 0.036$, we can calculate that more than 98% is present as $CuCl_4^{2-}$ in 6.2 M $CaCl_2$.

Systems such as the $CuCl_2$ system with the same characteristic coordination number and magnetism for the aqua ion and the chloro complexes normally have a rather constant, partly statistically determined ligand effect.[9] Ramette and Fan[1] criticize the fact that this assumption is involved in our calculations. However, the assumption is in agreement with the findings of Schwing-Weill et al.,[3,4] and it looks more suspicious that the stability constants calculated from Ramette's solubility measurements show a far from constant ligand effect; cf. Table I.

The basis for our recalculations is the fact that $CuCl_4^{2-}$ is the only absorbing species at 436 nm at sufficiently high chloride concentrations. This can be seen directly from the measurements made by Spacu and Murgulescu.[10] These authors made measurements on $CuCl_2$ solutions with increasing concentrations of KCl, and their data have subsequently been confirmed and analyzed.[5] Moeller[11] applied Job's "Mêthode des Variations Continuées" and examined mixed equimolar solutions of 2–4 M $CuCl_2$ and 2–4 M of LiCl, NaCl, and KCl in the wavelength range from 440 to 480 nm. Moeller found a pronounced maximum for the 1–4 complex for all chlorides investigated, again showing that the tetrachloro complex dominates the absorbance in this wavelength range. Some additional absorbance measurements on $CuCl_2$ solutions in the blue visible region with the chloride concentrations varying from 4 up to 5.35 M (saturated NaCl) made by us to emphasize this point are shown in Table II. From the previously determined values[2] for $\epsilon_\lambda{}^\circ$ in 6.2 M $CaCl_2$, the values of the degree of formation of the tetra complex $\alpha_4 = \epsilon_\lambda/\epsilon_\lambda{}^\circ$ have been calculated in the wavelength range studied. These values are remarkably constant considering the large variation in the absorbance in the wavelength range in question. This strongly supports our assumption that $\alpha_4 \cong [CuCl_4^{2-}]/C_{Cu}$ and that $CuCl_4^{2-}$ is the only absorbing species at 436 nm. Under these conditions the following relation[2] should be valid:

$$\frac{\Delta \log \epsilon_\lambda}{\Delta \log [Cl^-]} = 4 - \bar{n}$$

The values of $\bar{n}$, the average number of ligands coordinated to the metal ion, calculated from this expression by combination of data for solution IV with those for solutions II and III are shown in Table II. These values show clearly that $\bar{n}$ determined in this way is surprisingly sensitive to changes in the medium considering the small differences in the $NaClO_4$ concentration in solutions II and III (with C_{NaClO_4} respectively 0.50 and 0.75 M). On the other hand, the values of $\bar{n}$ in the two cases are relatively independent of the wavelength of calculation, and it can also be seen that their average values at 436 nm, 1.84 and 2.45, respectively, are not far from our value of 2.14 for 5 M NaCl in Table III of ref 2.

In order to examine how far the 5 M $Na(Cl,ClO_4)$ medium can be considered to be a "constant" medium, we have made solubility measurements on $Ca(IO_3)_2{\cdot}6H_2O$ at 25.0 °C. Our results are compared in Figure 1 with the solubility data of Ramette and Fan for $Cu(IO_3)_2{\cdot}{}^2/_3H_2O$. It can be seen that changing the NaCl concentration from 0 to 5 M in the 5 M $Na(Cl,ClO_4)$ medium causes a considerable increase in the solubility of $Ca(IO_3)_2$. Our experimental results at 25 °C can be expressed by the empirical formula $C_{Ca(IO_3)_2} = 0.0139 + 0.0042C_{NaCl}$.

The determination of stability constants by solubility measurements with a slightly soluble salt is a good method provided that the salt medium is sufficiently constant.[12] These conditions are fulfilled fairly well in the cadmium bromide system, for which Ramette[13] has obtained good values for the stability constants in 3 M $Na(ClO_4,Br)$. In the latter medium the formation of the final tetrabromo complex is half complete when 3 M $NaClO_4$ is replaced by 2.5 M $NaClO_4$/0.5 M NaBr. However, it is much more drastic to change the medium completely from 5 M $NaClO_4$ to 5 M NaCl. From the increase in the solubility of $Ca(IO_3)_2$ observed on changing the medium in this manner it is of course possible to calculate fictive equilibrium constants for calcium chloride complexes, but in our opinion the increase in solubility is due to a medium effect. In support of this it can be mentioned that a careful spectrophotometric study by Heistand and Clearfield[14] has made possible the determination of the concentration constant $K_1 = [FeCl^{2+}]/([Fe^{3+}][Cl^-])$ in 5 M $(Na,H)ClO_4$ medium, and it was found that K_1 increases from 20 ± 4 in 4 M $NaClO_4$/1 M $HClO_4$ to 48 ± 7 in 5 M $HClO_4$. The term ionic strength is well-defined and useful up to 0.1 M, but the Debye–Hückel theory indicates that it has little value in strong salt solutions. For this reason Bjerrum in 1946,[5] as well as with Skibsted in 1975,[7] studied weak complex formation in individual complex-forming electrolytes up to the highest possible concentrations.

Finally, it should be mentioned that Ramette and Fan appear to be unfamiliar with the high constancy of ligand field spectra relative to electron-transfer bands with respect to changes in medium.[6] These authors find that a considerable shift in the absorption maximum of the bis(ethylenediamine)copper(II) complex from 538 to 551 nm occurs when the medium is changed from 5 M $NaClO_4$ to 5 M NaCl while at the same time the molar absorbance increases about 15%. This result is confirmed by us, but it is not a simple medium effect. It is a consequence of the fact that the bis(ethylenediamine) complex in the strong chloride solution is partly converted to $Cu(en)_2Cl^+$. Due to this complex formation, the molar absorption increases and the maximum shifts toward higher wavelengths.[15,16] This happens not only when tetraamine copper(II) ion forms pentacoordinated complexes by uptake of amines but also when complex-forming anions bind to

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(1) Ramette, R. W.; Fan, G. *Inorg. Chem.* **1983**, *22*, 3323–6.

(2) Bjerrum, J.; Skibsted, L. H. *Acta Chem. Scand., Ser. A* **1977**, *A31*, 673–7.

(3) Schwing-Weill, M. J. *Bull. Soc. Chim. Fr.* **1973**, 823–30.

(4) Khan, M. A.; Schwing-Weill, M. J. *Inorg. Chem.* **1976**, *15*, 2202–5.

(5) Bjerrum, J. *Mat.-Fys. Medd.—K. Dan. Vidensk. Selsk.* **1946**, *22*,(18), 1–41.

(6) Bjerrum, J.; Adamson, A. W.; Bostrup, O. *Acta Chem. Scand.* **1956**, *10*, 329–31.

(7) Bjerrum, J.; Halonin, A. S.; Skibsted, L. H. *Acta Chem. Scand., Ser. A* **1975**, *A29*, 326–32.

(8) Skibsted, L. H.; Bjerrum, J. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 429–34.

(9) Bjerrum, J. *Metal Ammine Formation in Aqueous Solution*, 2nd ed.; P. Haase: Copenhagen, 1957.

(10) Spacu, G.; Murgulescu, J. G. *Z. Phys. Chem., Abt. A* **1934**, *170*, 71–80.

(11) Moeller, T. *J. Phys. Chem.* **1944**, *48*, 111–9.

(12) Bjerrum, J. *K. Tek. Hoegsk. Handl.* **1972**, *No. 253*, 71–7.

(13) Ramette, R. W. *Anal. Chem.* **1983**, *55*, 1232–6.

(14) Heistand, R. N.; Clearfield, A. *J. Am. Chem. Soc.* **1963**, *85*, 2566–70.

(15) Romano, V.; Bjerrum, J. *Acta Chem. Scand.* **1970**, *24*, 1551–60.

(16) Bjerrum, J.; Agarwala, B. V. *Acta Chem. Scand., Ser. A* **1980**, *A34*, 475–81.

Table I. Consecutive Stability Constants and Ligand Effects for Copper(II) Chloro Complex Formation in 5 M Na(Cl,ClO$_4$) at 25 °C

$$L_{n,n+1} = \log (K_n/K_{n+1}) - S_{n,n+1}$$

$$S_{1,2} = S_{3,4} = 0.426 \qquad S_{2,3} = 0.352$$

ref	K_1	K_2	K_3	K_4	$L_{1,2}$	$L_{2,3}$	$L_{3,4}$
3, 4	4	1.2	0.42	0.12	0.097	0.104	0.118
2	1.5	0.42	0.14	0.036	0.127	0.125	0.164
1	2.49	0.46	0.79	0.028	0.307	−0.59	1.02

Table II. Molar Absorbance of CuCl$_2$ Solutions in the Blue Visible Region at ~25 °C[a]

	wavelength, nm				
	420	430	436	440	450
I. C_{NaCl} = 4.00 M, C_{NaClO_4} = 1.00 M					
$\epsilon_\lambda{}^0$	548	380	308	263	168
ϵ_λ	24.4	15.8	12.0	9.95	5.96
α_4	0.044	0.042	0.039	0.038	0.035
II. C_{NaCl} = 4.50 M, C_{NaClO_4} = 0.50 M					
ϵ_λ	28.0	18.2	14.2	11.9	7.32
α_4	0.051	0.048	0.046	0.045	0.044
III. C_{NaCl} = 4.50 M, C_{NaClO_4} = 0.75 M					
ϵ_λ		20.0	15.6	13.2	8.13
α_4		0.053	0.051	0.050	0.048
IV. C_{NaCl} = 5.35 M, C_{NaClO_4} = 0.00 M					
ϵ_λ		25.1	19.8	16.6	10.3
α_4		0.066	0.064	0.063	0.061
$\bar{n}$(IV–II)		1.91	1.84	1.80	1.81
$\bar{n}$(IV–III)		2.52	2.45	2.51	2.49

[a] Measured on a Cary 219 spectrophotometer with the experimental condition described previously.[2]

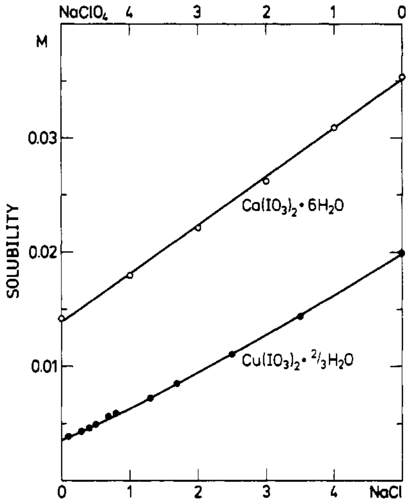

Figure 1. Solubility curve for Ca(IO$_3$)$_2$·6H$_2$O in 5 M Na(Cl,ClO$_4$) at 25 °C compared with the solubility curve for Cu(IO$_3$)$_2$ determined by Ramette and Fan[1] under the same conditions. Experimental conditions are as follows: The Ca(IO$_3$)$_2$·6H$_2$O employed was recrystallized and analyzed by iodate titration (purity 99.7 ± 0.2%). It was shaken with the salt medium in a thermostat, and equilibrium was found to be established after a few days. Powder X-ray diffractograms of the solid phases in equilibrium with 5 M NaCl and 5 M NaClO$_4$ that were isolated and dried at room temperature were identical with the diffractogram of a pure sample of Ca(IO$_3$)$_2$·6H$_2$O dried in a similar manner.

the tetraamine ion.[17] The spectrum of Cu(en)$_2$(H$_2$O)$^{2+}$ is practically the same in 5 M NaClO$_4$ as in dilute aqueous solution.

Registry No. Cu(IO$_3$)$_2$, 7789-80-2; NaCl, 7647-14-5; NaClO$_4$, 7601-89-0.

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(17) Romano, V., private communication.

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Copper(II) Complexes with Chloride Ion

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There are two reliable and independent equilibrium studies of copper(II) chloro complexes at ionic strength 5. One is a spectrophotometric study by Schwing-Weill,[1] later extended by Khan,[2] comprising a meticulous survey of 37 solutions ranging from 0.01 to 4.9 M sodium chloride, with measurements at 12 wavelengths in the UV and visible regions. By using an iterative computer algorithm, Khan and Schwing-Weill[3] found the best fit of the entire data set in terms of equilibrium constants for four successive complexes.

The other study,[4] from this laboratory, involved precise measurements of the solubility of copper iodate in a series of sodium chloride solutions up to 5 M. From ad hoc computer programs, the four β values were deduced to be significantly different from the spectrophotometric results, as shown in Table I.

Bjerrum and Skibsted opine[5] that both of these studies are lacking. They refer to the "suspiciously low value" for the molar absorptivity found by Khan and Schwing-Weill for the tetrachloro complex, and they suggest that the solubility approach suffers from medium effects as the solution composition varies from 5 M sodium perchlorate to 5 M sodium chloride. They have not addressed the obvious idea that the activity coefficients of the copper species in the spectrophotometric study are subject to exactly the same medium effects as in the solubility study. They have proposed[6] an alternative set of equilibrium constants (Table I) chosen to support their assumptions about the nature of copper(II) in the virtually nonaqueous medium of 6.2 M calcium chloride and their expectation of a nearly constant ligand effect.[11] We contend that such an approach is not a valid substitute for accurate experimental studies that can stand on their own.

At the time the solubility study was published, we were not yet appreciative of the power and value of nonlinear regression as a technique to deconvolute complex data. A good discussion of the application of this approach to chemical data has been given by Meites.[7] It includes proper weighting of data points and provides a least-squares fit based on the actual raw data. Because of Bjerrum and Skibsted's concern that the results from the solubility study show an unusual ligand effect, it seemed worthwhile to recalculate the solubility data by using nonlinear regression.

This technique involves making initial guesses of the four β values and using these to predict the solubility of copper iodate in each of the chloride solutions. The program then systematically refines the guesses until the fit is optimized. The resulting β values differ somewhat from those we published[4] and are to be preferred. They are 2.36 (0.07), 1.49 (0.19), 0.69 (0.13), and 0.055 (0.021) where the standard errors are shown in parentheses. The corresponding stepwise constants and calculated ligand effects are shown in Table I.

The next question was whether the spectrophotometric data of Khan[2] would yield different β values if subjected to nonlinear regression. At the wavelength of 230 nm Khan made measurements over the full range of chloride concentrations. Here it is necessary to make initial guesses of eight parameters for a given wavelength, the four β values and the four molar absorptivities of the complexes. The molar absorptivity of the uncomplexed copper ion is available from direct measurement in 5 M sodium

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(1) Schwing-Weill, M. J. *Bull. Soc. Chim. Fr.* **1973**, 823–30.
(2) Khan, M. A. Ph.D. Thesis, Universite Louis Pasteur de Strasbourg, 1975.
(3) Khan, M. A.; Schwing-Weill, M. J. *Inorg. Chem.* **1976**, *15*, 2202–5.
(4) Ramette, R. W.; Fan, G. *Inorg. Chem.* **1983**, *22*, 3323–6.
(5) Bjerrum, J.; Skibsted, L. *Inorg. Chem.*, preceding paper in this issue.
(6) Bjerrum, J.; Skibsted, L. *Acta Chem. Scand. Ser. A* **1977**, *A31*, 673–7.
(7) Meites, L. *CRC Crit. Rev. Anal. Chem.* **1979**, *8*, 1–53.