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49. Stabilities and Near UV. Charge Transfer Spectra of Binuclear and Heterobinuclear Complexes of N,N'-bis-[2-(2-pyridylmethylamino)-ethyl]-oxamide with Transition-Metal Ions

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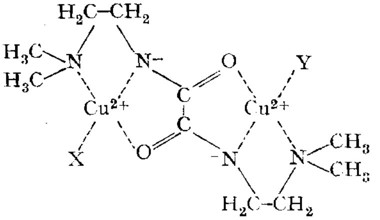
(9. X. 72)

Summary. The formation of complexes of N,N'-bis-[2-(2-pyridylmethyl-amino)-ethyl]-oxamide ($PAOH_2$) with Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} has been studied potentiometrically and spectrophotometrically. Besides mononuclear species, $PAOH_2$ forms the binuclear or heterobinuclear complexes $Cu_2(PAOH_2)^{4+}$, Cu_2PAO^{2+}, Zn_2PAO^{2+}, $CuNiPAO^{2+}$, and probably $CuZnPAO^{2+}$. Some of these five compounds show an UV. absorption band near 350 nm reminiscent of that of dimeric copper acetate. The results suggest that charge transfer from the oxamidato group to Cu^{2+} is responsible for the near UV. absorption.

N,N'-Bis-(2-dimethylamino-ethyl)-oxamide ($DEOXH_2$) [1] [2] and related compounds [3] [4] easily form binuclear copper complexes. Structure I has been verified



I

X, Y: Monodentate ligands such as H_2O or OH^-, SCN^-, CN^-, etc.

by X-ray analysis of the dithiocyanate $Cu_2DEOX(SCN)_2 \cdot 2DMF$ crystallised from dimethylformamide [5]. These binuclear complexes and dimeric copper acetate (Cu-Cu distance = 2.64 Å [6]) have in common: a relatively weak UV.-band near 350 nm and spin-spin interaction of the copper atoms as deduced from ESR. and magnetic susceptibility. As the properties of dimeric alkanoates have attracted considerable attention (see e.g. [7] [8]), we thought it worth-while to search for ligands that would form binuclear or heterobinuclear complexes of the general structure I with metal ions other than Cu^{2+}.

In the present paper, the stability constants and absorption spectra of the complexes formed by N, N′-bis-[2-(2-pyridylmethyl-amino)-ethyl]-oxamide ($PAOH_2$) with Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} or Zn^{2+} are reported.

Experimental. – *N, N′-Bis-[2-(2-pyridylmethyl-imino)-ethyl]-oxamide (PIO).* 8 mmoles of freshly distilled pyridine-2-aldehyde (*Fluka*) in 10 ml methanol were added dropwise to a stirred solution of 4 mmoles of N, N′-bis-(2-aminoethyl)-oxamide [9] in 40 ml CH_3OH. Within a few minutes the di-imine precipitated in analytically pure form. Yield 75%, m.p. 186/7°.

$C_{18}H_{20}N_6O_2$ Calc. C 61.39 H 5.72 N 23.85% Found C 61.68 H 5.92 N 23.80%

N, N′-Bis-[2-(2-pyridylmethyl-amino)-ethyl]-oxamide tetrahydrochloride ($PAOH_2 \cdot 4HCl$). 500 mg of the di-imine (PIO) were dissolved in 70 ml tetrahydrofurane (THF) at 35° and hydrogenated at atmospheric pressure with 10% Pd/C as catalyst. After filtration of the catalyst and evaporation of the solvent, the residue was taken up in ethanol and the tetrahydrochloride precipitated with ethanolic HCl. Recrystallisation from 90% ethanol yielded 80% $PAOH_2 \cdot 4HCl$, m.p. 230/1°.

$C_{18}H_{28}Cl_4N_6O_2$ Calc. C 43.04 H 5.62 N 16.73 Found C 42.75 H 5.83 N 16.61%

Measurements and equipment. Reagents: analytical grade, used without further purification. Temperature: 25° ± 0.1°. Ionic strength: 0.1 (KCl). Potentiometric titration curves were obtained with a compensator E 388 (*Methrom*), fitted with glass and calomel electrodes, as reference. Suitable mixtures of PAO and the sulfates of Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} or Zn^{2+} were titrated in 40 ml 0.1 M KCl with NaOH Titrisol (*Merck*) under 99,99% N_2.

The deprotonation constants of the two pyridinium sites were calculated from near UV. absorption spectra of $6 \cdot 10^{-4}$ M solutions of PAO with pH 1.0–3.0. The stability constants of several copper complexes were obtained from plots of extinction against ligand or metal ion concentration. $2.77 \cdot 10^{-4}$ and $5.54 \cdot 10^{-4}$ M solutions of PAO each with 1 or 1.8 equivalents of Cu^{2+} were used to determine the absorption spectra of the copper complexes and to check the stability constants.

All absorption spectra were run on a *Cary* 14. Stability constants and spectra were calculated from the experimental data using a PDP9 digital computer and the programmes VARIAT and SPANA described elsewhere [10].

Results. – Some of the potentiometric titration curves are shown in Figs. 1–3. As the two amide hydrogens tend to ionise under the influence of some metal ions, $PAOH_2 \cdot 4HCl$ was considered to be a hexabasic acid LH_6 (charges omitted) for the mathematical treatment of the data. Besides the ligand protonation constants, seven equilibria (1)–(7) had to be considered. The pK^H values of PAO and the dissociation constants of the complexes are summarized in Tab. 1.

Table 1. *Deprotonation constants of* $PAOH_2 \cdot 4HCl$ *and dissociation constants of its complexes with* Co^{2+}, Ni^{2+}, *and* Cu^{2+}

Ligand		pK_1^H	pK_2^H	pK_3^H	pK_4^H	pK_5^H	pK_6^H	
deprotonation		1.25 [a]	1.85 [a]	6.83	7.79	– [b]	– [b]	
		pK_1	pK_2	pK_3	pK_4	pK_5	pK_6	pK_7
Complex	Co^{2+}	4.2 [c]	4.8 [c]	1.33	9.31	–	–	–
dissociation	Ni^{2+}	–	7.48	–1.95	10.58	–	–	–
	Cu^{2+}	7.65 [a]	11.10 [a]	–4.02 [a]	9.40	3.88 [a]	13.90	–
	Cu^{2+}/Ni^{2+}	–	–	–	–	–	–	8.84

[a] Values determined spectrophotometrically; otherwise obtained from potentiometric titration curves.

[b] > 12.

[c] Relatively uncertain values, species of minor significance.

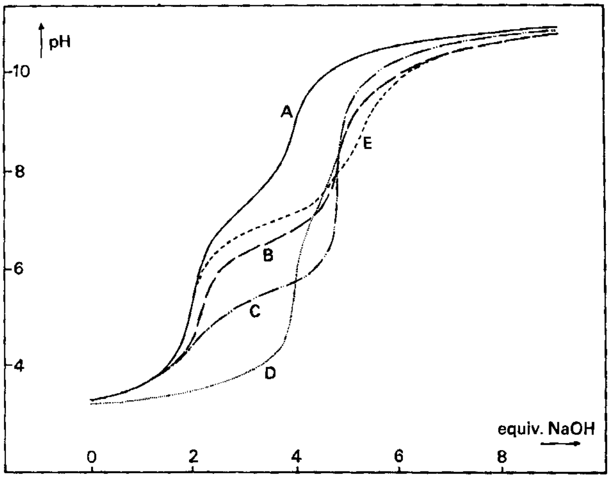


Fig. 1. *Potentiometric titration curves of N,N'-bis-[2-(2-pyridylmethyl-amino)-ethyl]-oxamide.* 1:1 mixtures of metal ion and PAO. [PAOH$_2$·4HCl]$_{tot}$ = 2.77·10^{-4}. ——— (A): no metal ion; — — — (B): [Co^{2+}]$_{tot}$ = 2.77·10^{-4}; —·—·—·· (C): [Ni^{2+}]$_{tot}$ = 2.77·10^{-4}; .... (D): [Cu^{2+}]$_{tot}$ = 2.77·10^{-4}; - - - - - - (E): [Zn^{2+}]$_{tot}$ = 2.77·10^{-4}.

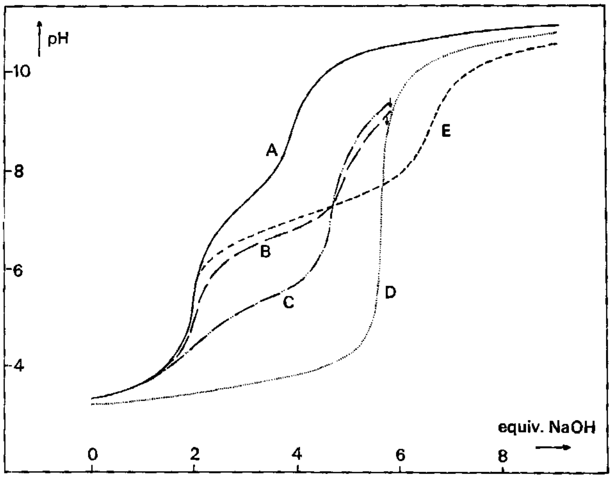


Fig. 2. *Potentiometric titration curves of N,N'-bis-[2-(2-pyridylmethyl-amino)-ethyl]-oxamide.* [Metal ion]$_{tot}$:[PAO]$_{tot}$ = 1.8:1. [PAOH$_2$·4HCl]$_{tot}$ = 2.77·10^{-4}. ——— (A): no metal ion; — — — (B): [Co^{2+}]$_{tot}$ = 5·10^{-4}; —·—·—·· (C): [Ni^{2+}]$_{tot}$ = 5·10^{-4}; .... (D): [Cu^{2+}]$_{tot}$ = 5·10^{-4}; - - - - - - (E): [Zn^{2+}]$_{tot}$ = 5·10^{-4}.

PAOH$_2$·4HCl loses its two pyridinium protons below pH 2. An apparent mean pK of 1.55 was calculated from spectrophotometric data at λ = 260 nm as described in [11]. Since the ligand is symmetric and no coulombic interaction between the two protons was observed, the statistical factor of 4 was used to obtain the individual values pK_1^H = 1.25 and pK_2^H = 1.85. pK_3^H and pK_4^H were determined from potentiometric data (cf. Fig. 1, curve A).

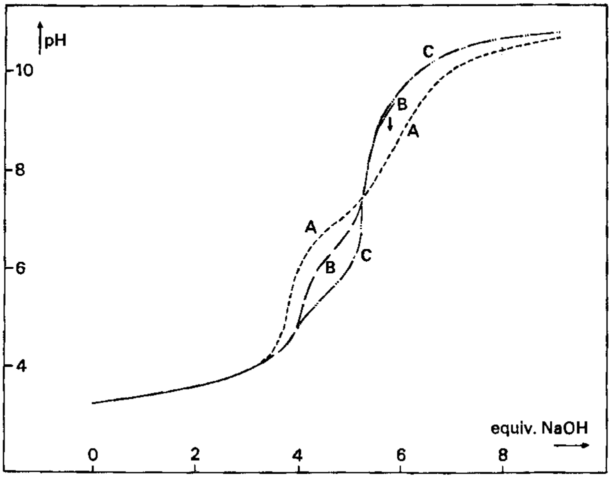


Fig. 3. *Potentiometric titration curves of N, N′-bis-[2-(2-pyridylmethyl-amino)-ethyl]-oxamide.* Formation of heterobinuclear complexes. $[PAOH_2 \cdot 4HCl]_{tot} = 2.77 \cdot 10^{-4}$, $[Cu^{2+}]_{tot} = 2.77 \cdot 10^{-4}$. ------ (A): $[Zn^{2+}]_{tot} = 2.22 \cdot 10^{-4}$; —— —— (B): $[Co^{2+}]_{tot} = 2.22 \cdot 10^{-4}$; —·—.. (C): $[Ni^{2+}]_{tot} = 2.22 \cdot 10^{-4}$.

$$MLH_3 \rightleftharpoons LH_3 + M \quad : K_1 = [M]\,[LH_3]/[MLH_3] \tag{1}$$

$$MLH_2 \rightleftharpoons LH_2 + M \quad : K_2 = [M]\,[LH_2]/[MLH_2] \tag{2}$$

$$M + LH_2 \rightleftharpoons MLH + H^+ \quad : K_3 = [MLH]\,[H^+]/[M]\,[LH_2] \tag{3}$$

$$MLH \rightleftharpoons ML + H^+ \quad : K_4 = [H^+]\,[ML]/[MLH] \tag{4}$$

$$M_2LH_2 \rightleftharpoons MLH_2 + M \quad : K_5 = [M]\,[MLH_2]/[M_2LH_2] \tag{5}$$

$$M_2L \rightleftharpoons ML + M \quad : K_6 = [M]\,[ML]/[M_2L] \tag{6}$$

$$CuNiL^{2+} \rightleftharpoons CuL + Ni^{2+} \quad : K_7 = [CuL]\,[Ni^{2+}]/[CuNiL^{2+}] \tag{7}$$

As can be seen from Fig. 1 and 2, 1:1 mixtures of PAO with Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} can be titrated over the whole pH range and stable binuclear complexes are formed with Cu^{2+} and Zn^{2+}. On the other hand, binding of Mn^{2+} was negligible, and with Fe^{2+}, partial precipitation occurred even in mixtures containing two moles of ligand per mole of Fe^{2+}; these two metal ions were therefore studied any further.

For Co^{2+} and Ni^{2+}, the calculation of the stability constants from potentiometric data was straightforward. $CuLH_3$ and $CuLH_2$ are formed well below pH 3, while $CuLH_2$ and CuLH are of minor importance as compared to Cu_2L, unless a considerable excess of ligand is used. Therefore, in order to obtain unambigious values of K_1, K_2, K_3, and K_5, describing the stability of $CuLH_3$, $CuLH_2$, CuLH, and Cu_2LH_2, spectrophotometric data had to be used. K_1 and K_5 were calculated from plots of E_{700} *vs.* metal ion (Fig. 4, curve A) or ligand (Fig. 4, curve B) concentration. Similarly, K_2 and K_3 were determined from plots of E_{590} *vs.* ligand concentration at pH 6.0 and 8.0, respectively. Potentiometric titration curves yielded the stability constants of CuL and Cu_2L. Because of partial hydrolysis the behaviour of the Zn^{2+} complexes is more

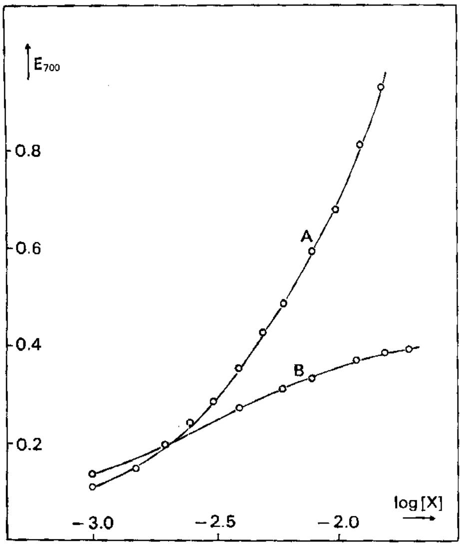


Fig. 4. *Spectrophotometric determination of the stability constants of* $CuLH_3$ *and* Cu_2LH_2. *pH* = *2.0*, *λ* = 700 nm, 4 cm cuvettes.
A: $[PAO]_{tot} = 2 \cdot 10^{-3}$, $[X]_{tot} = [Cu^{2+}]_{tot} = 10^{-3} - 2 \cdot 10^{-2}$; B: $[Cu^{2+}]_{tot} = 2 \cdot 10^{-3}$, $[X]_{tot} = [PAO]_{tot} = 10^{-3} - 2 \cdot 10^{-2}$. ○ exp., ——— calc.

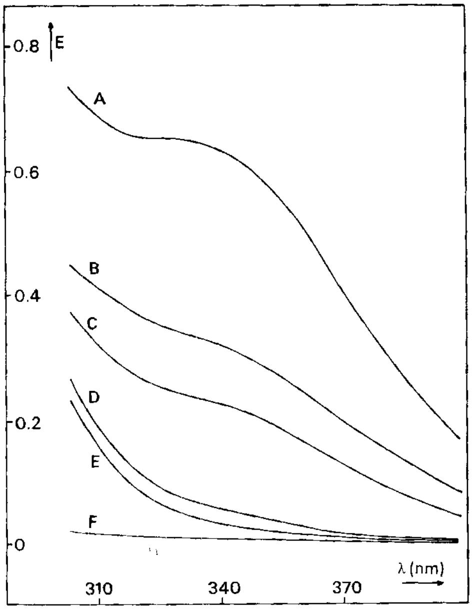


Fig. 5. *Near UV. absorption of complexes with N,N'-bis-[2-(2-pyridylmethyl-amino)-ethyl]-oxamide.* $[PAO]_{tot} = 2.5 \cdot 10^{-4}$, 4 cm cuvettes.
A: $[Cu^{2+}]_{tot} = 4.5 \cdot 10^{-4}$, pH = 6.0; B: $[Cu^{2+}]_{tot} = 2.5 \cdot 10^{-4}$, $[Ni^{2+}]_{tot} = 2 \cdot 10^{-4}$, pH = 9; C: $[Cu^{2+}]_{tot} = 2.5 \cdot 10^{-4}$, $[Zn^{2+}]_{tot} = 2 \cdot 10^{-4}$, pH = 8.9; D: $[Cu^{2+}]_{tot} = 10^{-2}$, pH = 2.5; E: $[Cu^{2+}]_{tot} = 2.5 \cdot 10^{-4}$, pH = 12.0; F: $[Zn^{2+}]_{tot} = 4.5 \cdot 10^{-4}$, pH = 9.0.

complicated, excluding a quantitative treatment, as they show no useful absorption bands.

Solutions containing Cu^{2+}, PAO, and Co^{2+}, Ni^{2+} or Zn^{2+}, respectively, rendered possible a study of the formation of heterobinuclear complexes. With Co^{2+} (cf. Fig. 3, curve B), precipitation occurs at pH 9, and the titration curve could be explained quantitatively without the assumption of heterobinuclear complexes. Mixtures with Ni^{2+} or Zn^{2+} (Fig. 3, curves A and C) instead of Co^{2+} are stable even at pH 11. The dissociation constant K_7 of $CuNiPAO^{2+}$ was calculated to be $10^{-8.84}$. The existence of $CuZnPAO^{2+}$, although probable, cannot be considered as definitely established, since curve A in Fig. 3 can be qualitatively described using a mixture of Cu_2PAO^{2+} and Zn_2PAO^{2+} and quantitative treatment was not feasible in view of the difficulties with Zn^{2+} alone.

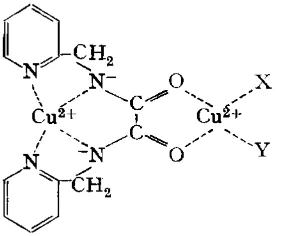
Table 2. d-d *absorption maxima* (λ_{max}) *and molar extinction coefficients* (ε) *of the* Cu^{2+} *complexes with PAO. The ε values are per mole of cupric ion.*

Species	$CuLH_3$	$CuLH_2$	CuLH	CuL	Cu_2LH_2	Cu_2L
λ_{max} (nm)	700	610	592	572	700	590
ε ($cm^{-1} M^{-1}$)	56	142	142	157	56	236

Absorption spectra of suitable solutions were used to calculate the spectra of each of the different Cu^{2+} complexes. The absorption maxima in the visible region are compiled in Table 2. Fig. 5 shows some of the relevant absorption curves between 300 and 400 nm.

Discussion. – For the mononuclear complexes with PAO, several structures are possible, most of which are discussed already in [1], where DEOX is the ligand, and they are of no further concern here. Like several simpler oxamide derivatives [1]–[4], PAO easily forms binuclear copper complexes. Probably due to the two additional basic sites of PAO, binuclear and heterobinuclear complexes with other metal ions are also observed.

With a dissociation constant of $10^{-13.90}$ (K_6, cf. Tab. 1), Cu_2PAO^{2+} is a very stable complex. Its formation is practically complete in solutions containing 2 moles of Cu^{2+} per mole of PAO for pH 4–11 and there is even over 80% in 1:1 mixtures at pH 4–8. In contrast to Cu_2DEOX, hydrolysis of Cu_2PAO^{2+} to $Cu_2PAO(OH)^+$ and $Cu_2PAO(OH)_2$ is negligible below pH 11, which indicates that the two pyridylmethyl groups form additional chelate rings and block the co-ordination sites occupied by X^1 and X^2 in I. The shift of the visible absorption maximum from 660 nm in Cu_2DEOX^{2+} [1] to 590 nm in Cu_2PAO^{2+} (see Tab. 2) is completely in line with this. *Ojima et al.* [4] have assigned structure II rather than I to their binuclear oxamidatocopper(II) complexes. Although II might be probable with dipyridyl as a second chelating ligand, none of our systems could be explained in this way. Leaving aside the X-ray analysis of $Cu_2DEOX(SCN)_2 \cdot 2DMF$ [5], the Cu^{2+} ion which is co-ordinated exclusively to oxygen atoms in II could only be rather loosely bound ($K_6 = 10^{-1}$–10^{-6}) and would be very susceptible to hydrolysis. In addition, the ligand fields of the two metal ions would be quite different from each other. Thus, the Cu^{2+} bound to 4 (DEOX) – or perhaps 6 (PAO) – nitrogen atoms would absorb around 550 nm and the other at 700–750 nm. In each of the binuclear complexes we have studied only one single *d-d* absorption band of normal width has been observed.



II

X, Y: monodentate (e.g. H_2O) or chelating ligands (e.g. α,α'-bipyridyl)

An especially interesting feature of the binuclear oxamidatocopper(II) complexes is the near UV. absorption around 350 nm, as in dimeric copper acetate. Several reasons for the presence of the 360 nm band in $Cu_2(CH_3COO)_4$ have been discussed:

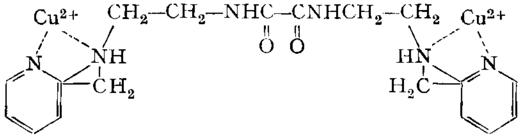
a) Direct linkage between the two central atoms [12],
b) charge transfer band according to (8) [1] [13], $Cu^{2+} \ldots Cu^{2+} \rightarrow Cu^{+} \ldots Cu^{3+}$ (8),
c) internal ligand transition band [14],

d) double ligand field excitation $(d_{z^2} \rightarrow d_{x^2-y^2}) \times 2$ [15],

e) ligand to metal charge transfer [8] [16].

a) can be completely excluded for Cu_2PAO^{2+} or Cu_2DEOX^{2+}, since the inter-copper distance is more than 5 Å in these complexes [5]. b) would imply that the position of the UV. band is sensitive to the nature of the ligands X and Y in I; indication of such sensitivity has already been observed [2]. According to c), the nature of the central atoms would be more or less irrelevant [14], whereas according to d) the UV. band should roughly have twice the energy of the 'normal' *d-d* transition; we should expect a considerable blue-shift for the UV. absorption in passing from $Cu_2(CH_3COO)_4$ ($\lambda_{max,\ visible}$ = 700 nm) and Cu_2DEOX^{2+} ($\lambda_{max,\ visible}$ = 660 nm) to Cu_2PAO^{2+} ($\lambda_{max,\ visible}$ = 590 nm). However, no such shift is found.

Whilst more evidence is needed to establish definitely the nature of the near UV. absorption in binuclear oxamidatocopper(II) complexes, the results obtained with PAO clearly suggest a ligand to metal charge transfer: Copper is essential, as Zn_2PAO^{2+} (Fig. 5, curve F) shows no absorption at all between 300 and 400 nm. Also, no UV. band above 300 nm is observed without deprotonation of the oxamide residue ($(Cu_2(PAOH_2)^{4+}$ (III), Fig. 5, curve D) or in absence of a dimeric structure($CuPAO^{2+}$, Fig. 5, curve E). On the other hand, based on the molarity of Cu^{2+}, $CuNiPAO^{2+}$ (Fig. 5, curve B) and possibly (cf. results) $CuZnPAO^{2+}$ (Fig. 5, curve C) have very nearly the same spectrum as Cu_2PAO^{2+} (Fig. 5, curve A). It thus appears that the near UV. band can be obtained without proximity of two Cu^{2+} ions, and that it does not reflect the interaction of the two metal ions which is observed by ESR. and magnetic susceptibility, but has its origin in the electron transfer from the organic ligand in the unusual electric field of two divalent metal ions to a single Cu^{2+}. The influence of the additional ligands X and Y [2] on the position of the near UV. band can also be easily explained by this mechanism.



III

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50. Radiolyse des hydrocarbures

20e communication[1]

n-Alcanes en phase liquide de l'heptane au dodécane

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(7 IX 72)

Summary. Effects of dose and temperature on the yields of the majority of the radiolysis products of the *n*-heptane, *n*-octane, *n*-nonane, *n*-decane and *n*-dodecane have been determined. The G-values of the products, excepting dimers are approximately the same for all the above *n*-alcanes. The temperature dependence, expressed as an apparent activation energy is shown to be equal for all *n*-alcanes.

1. Introduction. Les travaux entrepris dans les dix dernières années sur la radiolyse des hydrocarbures ont porté essentiellement sur le *n*-hexane et le cyclohexane. Ce dernier a été choisi car il contient seulement un type de liaison carbone-carbone et de liaison carbone-hydrogène, ce qui rend son étude analytique plus simple. L'hexane présente par contre l'avantage de pouvoir être irradié en phase liquide à des températures plus basses, où les réactions ayant une énergie d'activation non nulle sont négligeables. Les différentes liaisons carbone-carbone et carbone-hydrogène de l'hexane et des autres *n*-alcanes permettent aussi d'avoir un plus grand nombre de renseignements sur le comportement des hydrocarbures à la radiolyse. Les seules études présentant une analyse complète des produits de la radiolyse des *n*-alcanes portent sur le pentane [1] [2] et sur l'hexane [3] [4]. Les résultats différant notamment d'un auteur à l'autre, il est difficile de tirer des conclusions sur le comportement général des *n*-alcanes en radiolyse. Nous avons donc déterminé les rendements G_0 de la majorité des produits d'irradiation d'une série de *n*-alcanes (*n*-heptane, *n*-octane, *n*-nonane, *n*-décane et *n*-dodécane) dans un large domaine de température. L'influence de l'effet isotopique a été étudié dans le cas du *n*-dodécane. Nous nous sommes limités à classer les produits d'irradiation en différents groupes et à donner une valeur moyenne G_0(groupe) pour tous les *n*-alcanes irradiés. La variation de ces valeurs avec la température est exprimé en énergie d'activation apparente, calculée à partir de

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