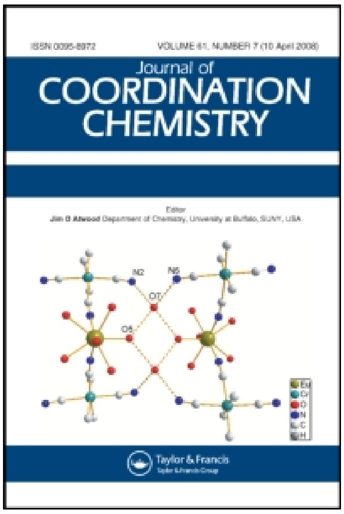

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SYNTHESIS AND CHARACTERIZATION OF SOME NITRO-SUBSTITUTED PHTHALOCYANINES OF NICKEL(II), COBALT(II) AND COPPER(II)

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Synthesis of the peripherally substituted (phthalocyaninato)metal derivatives $(NO_2)_4PcM$ (M = Ni, Co, Cu; NO_2 groups are in 1,8,15,22- or 2,9,16,23-positions) is described, and their X-ray powder diffraction patterns, solubilities, electronic and infrared spectra, and thermal stability are reported. The complexes exhibit isomorphism and polymorphism, and they are more soluble than the corresponding MPcs. Their thermal stability increases in the series Co < Ni < Cu, being at the same time greater for the 2,9,16,23-tetranitro- than for the 1,8,15,22-tetranitro derivatives.

Keywords: Nitrophthalocyanines, copper(II), cobalt (II), nickel(II), synthesis, properties

INTRODUCTION

Peripherally substituted metallophthalocyanines have been of interest in view of their use as redox catalysts,[1] in designing one-dimensional conductors,[2] and as photoconductors for electrophotography.[3,4] Although a variety of such complexes are known,[5-7] few nitro-derivatives have been characterized. Among the latter, the most extensively studied are (2,9,16,23-tetranitrophthalocyaninato)cobalt(II) ($4\text{-}NO_2CoPc$) and its bis(pyridine) adduct whose syntheses and physiocochemical properties have been reported.[2] There is a mention in the literature of the 1,8,15,22-tetraphthalocyaninato complexes of divalent cobalt, nickel, copper and iron, but very little is known concerning their preparation and properties.[8-11]

In this paper we present results on the synthesis, X-ray powder diffraction analysis, electronic and infrared spectra, and thermal stabilities of several nitro-substituted phthalocyaninato complexes of nickel(II), cobalt(II) and copper(II).

EXPERIMENTAL

The following compounds were prepared and purified by previously published procedures: 1) 4-nitrophthalic acid and 3-nitrophthalic acid;[12] 2) (2,9,16,23-tetranitrophthalocyaninato)cobalt(II),[2] except that 4-nitrophthalic acid instead of 4-nitrophthalic anhydride was used as one of the reagents; 3) unsubstituted metallophthalocyanines of cobalt(II), nickel(II) and coper(II).[13] Other reagents were commercially available and were of *p.a.* purity. Infrared spectra were recorded in the 4000–600 cm^{-1} range on a Perkin–Elmer 457 spectrophotometer in Nujol mulls.

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Electronic spectra were obtained on a Varian Superscan 3 spectrophotometer. Thermogravimetric measurements were carried out on a Perkin-Elmer Thermal Analysis Lab 1, TGS-2, FDC-1 instrument; heating rate 10°C/min, N_2 flow rate 60 cm^3/min. X-ray powder diffraction analysis was performed on a Philips PW 1051 Diffractometer, using CuKα radiation.

(1,8,15,22-Tetranitrophthalocyaninato)nickel(II)

3-Nitrophthalic acid (8.66 g, 0.041 mol), urea (10.33 g, 0.172 mol), nickel(II) chloride hexahydrate (3.09 g, 0.013 mol), and ammonium molybdate (0.2 g) were suspended in 44 cm^3 of nitrobenzene and heated at 190°C for 5 h. The resulting suspension was filtered hot and the filter cake washed with nitrobenzene and then with methanol. The cake was next suspended in 170 cm^3 of aqueous HCl ($c = 1$ mol/dm^3) and heated on a water-bath for 2 h, filtered, and washed with water until the filtrate was neutral. The treatment was repeated, but this time using 170 cm^3 of aqueous NaOH ($c = 1$ mol/dm^3) rather than HCl. The solid was finally suspended in methanol, filtered, and dried *in vacuo* at room temperature to a constant mass. This yielded 3.37 g (45%) of a dark blue-violet microcrystalline product (3-NO_2NiPc). *Anal.*; Calcd. for $C_{32}H_{12}N_{12}O_8Ni$: C, 51.16; H, 1.60; N, 22.38%. Found: C, 51.76; H, 2.15; N, 22.98%.

(2,9,16,23-Tetranitrophthalocyaninato)nickel(II)

The same procedure as above was employed except that 4-nitrophthalic acid instead of 3-nitrophthalic acid was used. The yield was 3.97 g (53%) of a blue-violet microcrystalline solid (4-NO_2NiPc). *Anal.*; Found: C, 49.94; H, 2.00; N, 23.25%.

(1,8,15,22-Tetranitrophthalocyaninato)cobalt(II)

The synthetic route was similar to that above except that cobalt (II) chloride hexahydrate (3.09 g, 0.013 mol) was used instead of $NiCl_2.6H_2O$. However, the work up as described above gave a rather impure material, so that the latter was next subjected to extraction by DMF. The resulting solution was vacuum-evaporated to dryness leaving behind 0.70 g (10%) of a dark blue-violet product (3-NO_2CoPc). *Anal.*; Calcd. for $C_{32}H_{12}N_{12}O_8Co$: C, 50.87; H, 1.35; N, 22.09%. Found: C, 51.15; H, 1.91; N, 21.05%.

(1,8,15,22-Tetranitrophthalocyaninato)copper(II)

The procedure was the same as above, except that copper(II) chloride dihydrate (2.15 g, 0.013 mol) was used instead of $CoCl_2.6H_2O$. The yield was 4.16 g (55%) of a blue-violet microcrystalline solid (3–NO_2CuPc). *Anal.*; Calcd. for $C_{32}H_{12}N_{12}O_8Cu$: C, 50.83; H, 1.58; N, 22.24%. Found: C, 50.31; H, 1.91; N, 20.07%.

(2,9,16,23-Tetranitrophthalocyaninato)copper(II)

The procedure was the same as above, except that 4-nitrophthalic acid instead of 3-nitrophthalic acid was used. The yield was 4.76 g (63%) of a blue-violet microcrystalline solid (4-NO_2CuPc). *Anal.*; Found: C, 50.42; H, 1.74; N, 20.01%.

X-ray Powder Diffraction Analysis

The results are listed in Table I.

TABLE I

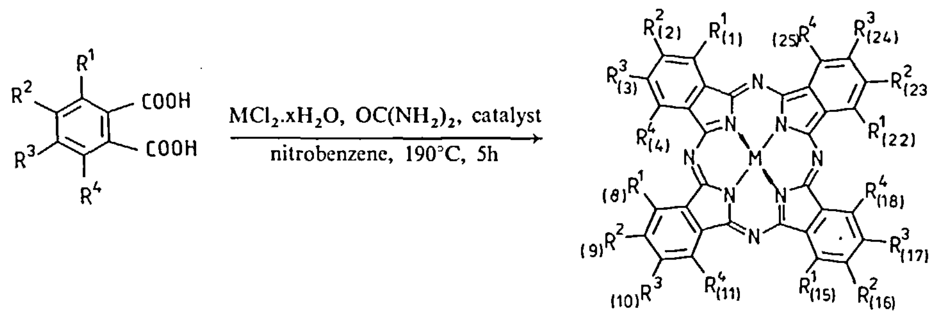
Relative intensities (%) and d-spacings (nm) of the X-ray powder diffraction maxima for nitro-substituted metallophthalocyanines.

3-NO_2NiPc		*4-NO_2NiPc*		*3-NO_2CoPc*		*4-NO_2CoPc*		*3-NO_2CuPc*		*4-NO_2CuPc*	
I	d	I	d	I	d	I	d	I	d	I	d
100	1.449							50	1.449		
100	1.381			3	1.360	60	1.400	60	1.280	60	1.360
		15	1.053	3	1.080			25	1.059		
19	1.028							24	1.028		
17	0.994							9	0.994		
		2	0.750	<1	0.790						
				1	0.737						
15	0.646					8	0.661	6	0.666	10	0.666
		5	0.624								
						7	0.607	5	0.591	6	0.591
								6	0.534		
10	0.519			2	0.514			8	0.516		
10	0.502							6	0.501		
		3	0.480	2	0.486						
								6	0.472		
8	0.462							5	0.462		
7	0.451										
								5	0.438		
3	0.402							7	0.410		
10	0.359							29	0.360	11	0.363
		5	0.341	3	0.336	20	0.347	15	0.345	20	0.344
45	0.339							32	0.335		
		15	0.324			52	0.328	42	0.328	50	0.324
4	0.306							3	0.303		
4	0.298										
				1	0.284						

RESULTS AND DISCUSSION

The syntheses of nitro-substituted metallophthalocyanines are summarized in Table II. The materials obtained exhibit relatively poor crystallinity. The X-ray powder diffraction patterns (Table I) suggest that 4-NO_2CuPc is isomorphous with 4-NO_2CoPc.[2] It also appears that 3-NO_2CuPc is a multiphase system containing similar crystalline phases as 3-NO_2NiPc and 4-NO_2NiPc. The presence of polycrystallinity is to be expected in these compounds since each of the syntheses of the tetranitro derivatives listed in Table II should theoretically yield a mixture of four isomers. This is because the R^2 and R^3 positions on the phthalic acid ring are mutually equivalent (as are the R^1 and R^4 positions), so that with one nitro group per benzene ring the four nitro groups in the resulting macrocycle can be scrambled in four different ways. [Calculations based on crystallographic data for MPcs[14] and nitrobenzene[15] show that no significant steric interaction between NO_2 groups would occur even in the least favourable case, *i.e.*, in the situation that two NO_2 groups are found in the closest possible proximity—in two adjacent sites such as (1) and (25) in the 1,8,15,22-isomer (Table II); the latter configuration would feature a distance between the O-atoms of the two NO_2 groups of at least twice the van der Waals radius for the O-atom (2.8 Å)].

TABLE II
Syntheses of nitro-substituted phthalocyanines of nickel(II), cobalt(II) and copper(II).



Product	Starting material	Yield (%)
$3\text{-}NO_2NiPc$	$R^1 = NO_2$; $R^2 = R^3 = R^4 = H$; $M = Ni$	45
$4\text{-}NO_2NiPc$	$R^2 = NO_2$; $R^1 = R^3 = R^4 = H$; $M = Ni$	53
$3\text{-}NO_2CoPc$	$R^1 = NO_2$; $R^2 = R^3 = R^4 = H$; $M = Co$	10
$3\text{-}NO_2CuPc$	$R^1 = NO_2$; $R^2 = R^3 = R^4 = H$; $M = Cu$	55
$4\text{-}NO_2CuPc$	$R^2 = NO_2$; $R^1 = R^3 = R^4 = H$; $M = Cu$	63

The solubility of the nitro-substituted metallophthalocyanines is more pronounced than that of the corresponding unsubstituted compounds. For example, $3\text{-}NO_2CuPc$ and $4\text{-}NO_2CuPc$ are soluble in DMF, DMSO and pyridine, whereas CuPc is not. The electronic spectral measurements were carried out on solutions of the nitro-substituted and the reference unsubstituted Ni(II)-, Co(II)-, and Cu(II)- phthalocyanines in both coordinating and noncoordinating solvents, and the results are listed in Table III. The data show that there is a perceptible electronic influence of the nitro groups on the substituted metallophthalocyanines so that both the presence of the groups as well as their location on the macro ring affect the position of the spectral maxima. The type of solvent also influences the spectra, and in some cases it affects the spectrum even more than does the presence of the ring substituents. For example, there is a greater shift of the strongest band in the visible spectrum (Q band) of $3\text{-}NO_2CoPc$ in *py* relative to its solution in ClN than there is for $3\text{-}NO_2CoPc$ in ClN (or *py*) relative to CoPc in ClN (or *py*). This is obviously due to effects of solvent coordination to the central cation; both the substituted and unsubstituted metallophthalocyanines are known to form mono- or bis(pyridine) adducts.[2] As to the effect of the above-mentioned possible presence of isomers in the tetranitro derivatives on spectral patterns, such effects appear to be very small; no significant broadening of the maxima is observed in the spectra of the tetranitrometallophthalocyanines (relative to spectra of MPcs), and the maxima could not be computer-resolved into possible isomer components.

TABLE III

Electronic spectral data for nitro-substituted and unsubstituted phthalocyanines of Ni(II), Co(II) and Cu(II) in 1-chloronaphthalene (ClN), DMF, DMSO and pyridine (*py*).

	λ_{max}, nm (relative optical density)			
Compound	ClN	DMF	DMSO	*py*
NiPc	670 (3.6) 620 (0.6) 602 (0.6) 340 (1.0)	680 (0.8) 614 (0.3) 340 (1.0)	680 (0.6) 610 (0.7) 330 (1.0)	670 (0.8) 606 (0.3) 330 (1.0)
3-NO_2NiPc	670 (3.1) 636 (0.6) 604 (0.6) 340 (1.0)	666 (0.6) 630 (0.5) 608 (0.5) 340 (1.0)	666 (0.5) 626 (0.4) 340 (1.0)	666 (1.4) 604 (0.7) 340 (1.0)
4-NO_2NiPc	690 (2.2) 620 (0.5) 340 (1.0)	680 (1.5) 626 (2.0) 470 (1.0)	690 (1.3) 630 (1.7) 470 (1.0)	680 (0.6) 630 (0.4) 340 (1.0)
CoPc	674 (3.4) 624 (1.0) 608 (0.6) 324 (1.0)	660 (1.3) 600 (0.3) 330 (1.0)	668 (2.1) 602 (0.5) 330 (1.0)	658 (1.7) 600 (0.4) 330 (1.0)
3-NO_2CoPc	669 (2.3) 604 (0.5) 340 (1.0)	706 (0.4) 653 (1.0) 595 (0.4) 316 (1.0)	655 (2.0) 595 (1.0)	657 (1.4) 598 (0.5) 340 (1.0)
4-NO_2CoPc	683 (2.0) 618 (0.5) 340 (1.0)	670 (0.9) 616 (0.6) 314 (1.0)	673 (1.3) 615 (0.5) 330 (1.0)	671 (1.8) 610 (0.6) 440 (0.3) 340 (1.0)
CuPc	684 (1.8) 652 (0.6) 614 (0.6) 588 (0.2) 568 (0.1)			
3-NO_2CuPc	680 (3.2) 647 (0.5) 601 (0.6) 340 (1.0)	669 (1.9) 604 (0.6) 344 (1.0)	670 (1.3) 625 (1.3) 605 (0.7) 340 (1.0)	673 (2.9) 606 (0.6) 340 (1.0)
4-NO_2CuPc	692 (2.3) 621 (0.6) 566 (0.1) 340 (1.0)	692 (0.4) 670 (0.4) 608 (0.7) 340 (1.0)	673 (0.6) 628 (0.6) 576 (0.3) 340 (1.0)	687 (0.8) 678 (0.8) 638 (0.3) 620 (0.3) 340 (0.7) 304 (1.0)

Infrared spectra of the products agree well with the presence of NO_2 groups on the Pc ring (Table IV). Both the asymmetric and symmetric N–O stretching bands are found in regions characteristic of aromatic nitro compounds.[16–18] The relative position of the NO_2 group on the ring does not seem to influence the N–O stretching frequencies. Some variation is evident only in the C–NO_2 bands, and it is mainly manifested through differences in relative band intensities (Table IV).

TABLE IV
NO_2 stretching frequencies in the infrared spectra of nitro-substituted phthalocyanines of Ni(II), Co(II) and Cu(II).

Compound	$\bar{\nu}_{as}$(N-O) (cm^{-1})	$\bar{\nu}_{s}$(N-O) (cm^{-1})	$\bar{\nu}$(C-NO_2) (cm^{-1})
3-NO_2NiPc	1525(vs)*	1340(vs)	855(w)
4-NO_2NiPc	1525(s)	1340(s)	850(m,b)
3-NO_2CoPc	1525(s)	1340(s)	855(w)
4-NO_2CoPc	1525(s)	1340(s)	855(m)
3-NO_2CuPc	1530(s)	1340(s)	890(w)
4-NO_2CuPc	1520(s)	1335(vs)	850(s)

* vs = very strong; s = strong; m = medium; w = weak; b = broad

Thermal stability of substituted metallophthalocyanines is generally known to be lower than that of corresponding MPc complexes.[1] The same behaviour is encountered in the nitro-substituted derivatives (Table V).

TABLE V
Thermogravimetric data for nitro-substituted and unsubstituted phthalocyanines of Ni(II), Co(II) and Cu(II).

Compound	decomposition temperature, °C	mass loss		fragment lost
		% found	% calcd	
3-NO_2NiPc	115–240	6.0	6.1	NO_2
	385–460	18.3	18.4	3 NO_2
4-NO_2NiPc	385–470	17.5	18.4	3 NO_2
	470–800	17.5		
NiPc*	455–650	46.0		
3-NO_2CoPc	25–130	12.7	12.2	2 NO_2
	130–285	6.7	6.1	NO_2
	385–720	33.5		
4-NO_2CoPc	90–330	6.2	6.1	NO_2
	330–450	17.1	18.4	3 NO_2
CoPc*	450–710	84.5		
3-NO_2CuPc	390–455	19.0	18.3	3 NO_2
	455–750	19.0		
4-NO_2CuPc	420–460	20.0	18.3	3 NO_2
	460–750	35.5		
CuPc*	545–660	27.7		
	660–800	27.2		

* Partly sublimes above 500°C.

Whereas NiPc, CoPc and CuPc begin to decompose only above 450°C, their NO_2-counterparts lose mass at much lower temperatures. The relative thermal stability of NO_2-phthalocyanines (as well as that of the parent MPcs) increases in the series Co < Ni < Cu with the 3-derivative generally being less stable than the 4-derivative. The latter result is not surprising in view of the possible steric interaction between the 3-NO_2 group and the macrocycle ring; assuming free rotation around the C-NO_2 bond, the distance between the O-atom and the N-atom forming the macrocycle aza bridge varies between 3.29 and 2.12 Å.

In conclusion, the results of the present work show that the nitro-substituted phthalocyanines of Ni(II), Co(II) and Cu(II) tend to exhibit isomorphism or polymorphism. The solubility of the complexes in characteristic organic solvents is greater than that of the corresponding MPcs. Their solution electronic spectra are influenced both by solvent and by the position of the NO_2-group on the aromatic ring. In addition, the NO_2 frequencies in the infrared spectra show no dependence on the position of the group on the ring, a slight dependence being evident only for the C–NO_2 band. Finally, the thermal stability of the nitro-substituted MPcs decreases in the series Co < Ni < Cu, and is also greater for the 4- than the 3-derivatives.

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