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THE HEAT STABILITIES OF SOME POLYMERIC METAL COMPLEXES*

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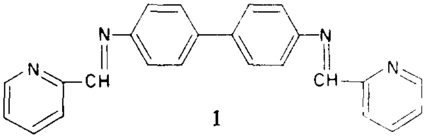
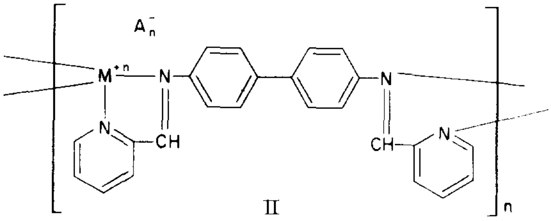
Abstract—Heat stability data are reported for a series of polymeric complexes of bis-(2-pyridinal)-biphenylene-4,4′-diimine. The salts which have been shown to give polymers are nickel(II) sulphate, zinc(II) nitrate and the following divalent metal chlorides and nitrates: iron, cobalt, nickel, copper, cadmium and mercury. In general, the metal nitrate polymers do not lose weight below 200°, the metal chloride polymers below 250°, and nickel(II) sulphate polymer below 300°C.

To date, most efforts to prepare coordination polymers have involved the use of organic chelating agents which simultaneously satisfy charge and fill the coordination positions of the metal ion. This study was undertaken to examine the heat stabilities of some coordination polymers in which the organic chelating agent does not neutralize the charge on the metal ion. bis-(2-Pyridinal)-biphenylene-4,4′-diimine(I) was chosen as the chelating agent because



I

(1) It can satisfy acceptor sites on metal atoms but it cannot satisfy their charge. Linear polymeric metal complexes of this chelating agent have the structure shown in II.



II

Here M represents a metal atom having a positive charge $+n$ and A is some monovalent anion which is not part of the chelating agent. Since the chelating agent does not neutralize charge, an anion must be present to neutralize the positive charge of the metal ions.

(2) Molecular models show that there is little possibility of forming a cyclic chelate as shown in III. Bond angles and steric requirements are such that the cyclic structure shown in III seems less likely than the polymeric structure shown in II. Molecular

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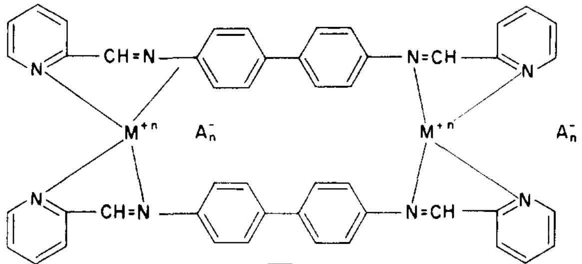
models also show that there is little evidence for expecting a cross-linked polymer when a hexa-co-ordinate metal such as Fe(II) or Co(II) is used. When three of these chelating groups approach a metal ion, each group prevents the other two from closely approaching the metal ion. However, the models show that two of these chelating groups can closely approach a metal ion having octahedral, tetrahedral or planar stereochemistry.



III

(3) The use of the biphenylene functional group avoids the thermal instability of saturated carbon chains. It also imposes a steric situation which lessens the possibility of forming a cyclic chelate as shown in III.

(4) The use of the pyridinal group allows conjugation in the five-membered chelate ring and possible double bonding with the metal atom. The presence of this conjugation or π-bonding may lead to greater heat stability. Since the (C=N) azomethine linkage is a member of a chelate ring, the presence of resonance in this chelate ring can be determined from the magnitude of the C=N stretching frequency. Any π-bonding in this five-membered ring tends to lower the C=N stretching frequency as compared to that of the free base.

The metal sulphates, chlorides and nitrates used in conjunction with (I) to form polymers are listed in Table 2. It was realised that polymers containing the nitrate ion would not be thermally stable. However, it seemed desirable to compare the chloride and nitrate polymers to see whether the same relative order of heat stabilities was displayed by both series. The chloride and nitrate ions were chosen because the former is a good donor and the latter is a bad donor. The heat stability data (Table 2) show the effect of different anions in polymers which contain the same chelating agents and metal ions.

DISCUSSION

1. *Preparation of compounds*

The polymeric complexes were prepared by bringing together methanol solutions of the chelating agent and the appropriate metal salt. In some instances, solid formed during the addition of metal salt and in other instances [$NiCl_2$, $Fe(NO_3)_2$, $Co(NO_3)_2$, $Ni(NO_3)_2$, $Cu(NO_3)_2$], the polymer remained in solution even after all of the salt had been added. Evaporation of the reaction mixtures to dryness led to solid polymeric products which were washed with acetone in a Soxhlet extractor, dried, and analysed.

When acetone or ethanol were used as reaction solvents, solids formed immediately after the metal salt was first added to the chelating agent. Chemical analysis for these solids agree well with those calculated for complexes showing metal to ligand ratios between 4:3 and 3:2.

All of the polymeric products prepared for this study are coloured, hygroscopic solids. This hygroscopic nature accounts in part for the differences between the analytical values calculated and those found. In general, hydrogen values are high and carbon and metal values are low. Chemical analyses for the polymeric complexes of copper(II)chloride and nickel(II)sulphate show that one molecule of water is associated with the repeating unit in the polymer.

A polymeric zinc(II) chloride complex could not be obtained by using the procedure which led to the other polymers. Attempts to prepare the zinc chloride polymer in methanol gave a complex having a metal to ligand ratio of two to one (empirical formula: $C_{24}H_{18}N_4.2ZnCl_2$).

The copper(II) nitrate polymer can be pulled into threads and the nickel(II) chloride polymer forms a putty-like solid just before the respective reaction mixtures are freed of methanol. After the methanol has evaporated, a glassy brittle solid is left in the case of the copper(II) nitrate polymer and a powder in the case of the nickel(II) chloride polymer. When the methanol reaction mixtures of the other polymers are freed of methanol, brittle glasses or finely divided solids remain. After drying, all of the glassy solids can be reduced to fine powders by grinding. The adhesive properties are temporary and depend on the presence of a small amount of methanol which acts as a plasticizer.

TABLE 1.—POLYMER SOLUBILITY*

Polymer	Water	Dimethyl-formamide	Dimethyl-Sulphoxide	Pyridine	Benzene	Tetrahydrofuran	Methanol
$FeCl_2$	*p*	*s*	*s*	*s*	*i*	*p*	*p*
$CoCl_2$	*s*	*s*	*s*	*s*	*i*	*i*	*p*
$NiCl_2$	*s*	*p.m.*	*s*	*s*	*i*	*i*	*p*
$CuCl_2$	*p.m.*	*p.m.*	*p.m.*	*s*	*i*	*i*	*p*
$CdCl_2$	*p.s.*	*p*	*s*	*s*	*i*	*p.s.*	*p*
$HgCl_2$	*i*	*s*	*s*	*s*	*p.s.*	*p*	*p*
$Fe(NO_3)_2$	*p*	*s*	*s*	*p*	*i*	*p*	*p*
$Co(NO_3)_2$	*p*	*s*	*s*	*s*	*i*	*i*	*p*
$Ni(NO_3)_2$	*s*	*s*	*s*	*p.m.*	*i*	*i*	*p*
$Cu(NO_3)_2$	*p*	*p*	*s*	*p*	*i*	*i*	*p*
$Zn(NO_3)_2$	*p*	*s*	*s*	*s*	*p.s.*	*p.s.*	*p*
$Cd(NO_3)_2$	*p*	*p*	*s*	*s*	*i*	*i*	*p.s.*
$Hg(NO_3)_2$	*p*	*p.m.*	*s*	*s*	*i*	*i*	*p*
$NiSO_4$	*s*	*p*	*p*	*p*	*i*	*i*	*p*

* Abbreviations
s—soluble *i*—insoluble *p*—partly soluble
p.m.—partly soluble (almost all is soluble) *p.s.* —partly soluble (very little is soluble)

Qualitative solubility data for the polymers that were tested for heat stability are listed in Table 1. Each determination involved about 3 mg of polymer per 3 ml of solvent.

2. *Infra-red study*

STRATTON and BUSCH have studied the infra-red spectra obtained for metal complexes of 2-pyridinaldazine and 2-pyridinalmethylimine and assigned modes to all bands in the 1400–1700 cm^{-1} region of the spectra.(1) The C=N stretching frequencies displayed by the iron complexes are lower than for the uncomplexed ligands. This lowering of

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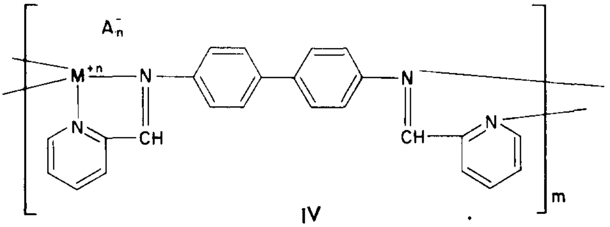
(1) W. T. STRATTON and D. H. BUSCH, *J. Amer. Chem. Soc.* **82**, 4834 (1960).

the C=N stretching frequency for the iron complexes is attributed to π-bonding in the chelate ring. Resonance in the chelate ring is expected to lead to a lower C=N stretching frequency because the bond order of the carbon-nitrogen bond is lowered. Possible π-bonding in the polymeric complexes was likewise studied by examining the infrared spectra in the 1500–1700 cm^{-1} region. The polymers show strong bands in the 1600 cm^{-1} region, slightly stronger bands in the 1500 cm^{-1} region and weak bands in the 1560 cm^{-1} region. These bands are attributed to aromatic ring vibrations of the pyridine and benzene rings.(2) The bands of medium intensity above 1625 cm^{-1} are due to the C=N stretching mode. With the exception of the iron(II) nitrate polymer, for which a C=N bond is not observed, all of the polymers display increased C=N stretching frequencies when compared to metal-free bis-(2-pyridinal)-biphenylene-4,4′-diimine. The C=N stretching frequency for the iron(II) nitrate polymer is possibly superimposed on the band at 1600 cm^{-1}. These results indicate some π-bonding in the chelate rings of the iron(II) nitrate polymer and no similar π-bonding for the other polymers.

3. *Heat stability determinations*

The thermogravimetric balance used for this study is similar to the one described by Winslow and Matreyek.(3) The polymeric products were dried for 12 hours at 140° in the balance and tested for heat stability in a nitrogen atmosphere. The data are reported in Table 2 as per cent weight loss over successive twelve hour periods at a

Table 2.—Heat stability data for polymeric metal complexes of bis-(2-pyridinal)-biphenylene-4,4′-diimine, (PBD).



IV

Metal M	Anion A	% Decomposed after Successive 12 hr periods at Designated Temperatures 250°	300°	350°	400°
Fe(II)	Cl	10·7	58·0		
Co(II)	Cl	0·58	8·80	46·0	
Ni(II)	Cl	1·70	5·50	34·5	
Cu(II)	Cl	3·06	12·5	44·0	
Cd(II)	Cl	0·00	5·30	34·0	
Hg(II)	Cl	3·70	11·0	46·0	
Fe(II)	NO_3	43·0			
Co(II)	NO_3	1·48	12·5		
Ni(II)	NO_3	2·0	27·0		
Cu(II)	NO_3	43·0			
Zn(II)	NO_3	2·4	50·0		
Cd(II)	NO_3	0·00	0·25	4·93	70·0
Hg(II)	NO_3	9·50	36·0		
Ni(II)	SO_4	2·50	2·50	7·10	20·4
Metal Free	PBD	0·70	3·00	17·0	

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(2) L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, p. 64–73. J. Wiley, New York (1958).

(3) F. H. Winslow and W. Matreyek, *J. Poly. Sci.* **22**, 315 (1956).

TABLE 3.—ANALYTICAL AND OTHER DATA FOR POLYMERIC COMPLEXES OF BIS-(2-PYRIDINAL)-BIPHENYLENE-4,4′-DIIMINE

Divalent cation	Anion	Analysis calc. for	C Calc.	C Found	H Calc.	H Found	Metal Calc.	Metal Found	*m.p.** (°C)	Yield (%)	Drying procedure†	Colour
Fe	Cl	$[C_{24}H_{18}N_4{\cdot}FeCl_2]_n$	59·0	58·5	3·68	3·99	11·4	11·4	>350°	—	1	Green
Co	Cl	$[C_{24}H_{18}N_4{\cdot}CoCl_2]_n$	58·5	58·0	3·66	3·99	12·0	10·0	>350°	80	1	Orange-yellow
Ni	Cl	$[C_{24}H_{18}N_4{\cdot}NiCl_2]_n$	58·6	57·9	3·66	3·84	11·9	10·9	>350°	93	2	Yellow-brown
Cu	Cl	$[C_{24}H_{18}N_4{\cdot}CuCl_2{\cdot}H_2O]_n$	56·0	55·3	3·89	3·88			212°	63	2	Yellow-brown
Cd	Cl	$[C_{24}H_{18}N_4{\cdot}CdCl_2]_n$	52·8	52·2	3·30	3·51			>350°	80	2	Yellow
Hg	Cl	$(C_{24}H_{18}N_4HgCl_2)_8HgCl_2$	43·2	43·0	2·70	2·65			243°d.	73	2	Yellow
Fe	NO_3	$[C_{24}H_{18}N_4{\cdot}Fe(NO_3)_2]_n$	53·2	52·7	3·32	3·15	10·3	8·16	200°d.	88	1	Lavender
Co	NO_3	$[C_{24}H_{18}N_4{\cdot}Co(NO_3)_2]$	52·8	53·1	3·30	3·47	10·8	9·8	>350°	86	2	Red-brown
Ni	NO_3	$[C_{24}H_{18}N_4{\cdot}Ni(NO_3)_2]$	52·8	52·7	3·30	3·51	10·8	9·8	>350°	89	3	Red-brown
Cu	NO_3	$[C_{24}H_{18}N_4{\cdot}Cu(NO_3)_2]$	52·3	52·5	3·28	3·38	11·5	11·5	>350°	—	3	Dark-brown
Zn	NO_3	$[C_{24}H_{18}N_4{\cdot}Zn(NO_3)_2]$	52·3	51·7	3·26	3·55	11·9	11·4	310°d.	86	3	Yellow
Cd	NO_3	$[C_{24}H_{18}N_4{\cdot}Cd(NO_3)_2]$	48·2	49·3	3·01	3·17			>350°	82	2	Yellow
Hg	NO_3	$[C_{24}H_{18}N_4{\cdot}Hg(NO_3)_2]$	41·0	40·4	2·84	2·83			>350°	71	2	Yellow
Ni	SO_4	$[C_{24}H_{18}N_4{\cdot}NiSO_4{\cdot}H_2O]_n$	53·8	54·3	3·36	4·11			>350°	—	2	Orange

* Abbreviations: d. decomposition.
† Abbreviations: 158° *in vacuo* (0.2 mm Hg).
2. 100° *in vacuo* (2·0 mm Hg).
3. 110° in the oven.

designated temperature (constant within ±3°). The data show many of these polymers to be stable at 250° and the nickel(II) sulphate and cadmium(II) nitrate polymer polymers to temperatures above 300°. Unfortunately, most of the polymers are less heat-stable than the metal-free chelating agent. Many of these polymers retain water after drying for four hours at 100° *in vacuo* (0·3 mm Hg); a weight loss of up to two per cent at 250° is probably due to loss of water. The heat stability of the cadmium nitrate polymer is certainly not expected when one considers the poor heat stability of the other nitrate containing ploymers,

The order of heat stability for the chloride containing polymers is $\mathrm{Cd(II)} \simeq \mathrm{Ni(II)} > \mathrm{Cu(II)} \simeq \mathrm{Co(II)} \simeq \mathrm{Hg(II)} \gg \mathrm{Fe(II)}$ and the order of heat stability for the nitrate containing polymers is $\mathrm{Cd(II)} \gg \mathrm{Co(II)} > \mathrm{Ni(II)} > \mathrm{Hg(II)} > \mathrm{Zn(II)} \gg \mathrm{Cu(II)} \simeq \mathrm{Fe(II)}$. The order of heat stability for the nickel polymers is $SO_4^{2-} > Cl^- > NO_3^-$. The data show that the relative orders of stability differ in the nitrate and chloride series. The presence of π-bonding in the chelate rings of the iron(II) nitrate polymer has no significant effect on the thermal stability of the polymer. The data also show that the anion strongly affects the stability of the nickel polymers.

EXPERIMENTAL

Bis-(2-Pyridinal)-biphenylene-4,4′-diimine

A warm solution of benzidene (m.p. 129–130°)(25·7 g, 0·1395 mole) in 200 ml of absolute ethanol was slowly added with stirring to a warm solution of pyridine 2-aldehyde* (30·0 g, 0·280 mole) in 50 ml of absolute ethanol. A yellow solid formed immediately. The reaction mixture was stirred for one half hour. Yield of crude solid after washing with ethanol and drying in air, 52·0 g (100 per cent). Yield of yellow needles after recrystallization from acetone, 23·3 g (46 per cent) m.p. 177–179°. Found: C, 79·4; H, 5·02. Calc. for $C_{24}H_{18}N_4$: C, 79·6; H, 4·98%).

Polymeric metal complexes of bis-(2-pyridinal)-biphenylene-4,4′-diimine (PBD)

All of the polymeric complexes were prepared by essentially the following procedure. Those which were tested for heat stability were prepared in methanol. Reagent grade metal salts were used without further purification. Chemical analyses and other pertinent data are listed in Table 3.

A warm solution of iron(II) chloride tetrahydrate (0·2740 g, 0·00138 mole) in approximately 40 ml of methanol was slowly added with vigorous stirring to a refluxing solution of bis-(2-pyridinal)-biphenylene-4,4′-diimine (PBD)(0·5000 g, 0·00138 mole) in 200 ± 10 ml of methanol. The ferrous chloride solution was added dropwise in four separate portions and the reaction mixture was allowed to reflux on the steam bath for 1–2 min after each portion of salt solution had been added. After all of the salt was added, the reaction mixture was evaporated to dryness on a steam bath to yield a green solid. This solid was dried in the oven at 110°C, and then extracted with acetone. The extracted product was dried in air and then *in vacuo.*

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* Pyridine-2-aldehyde (Aldrich Chemical Company) was used without further purification.