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THE PREPARATION, CHARACTERISATION AND THERMAL ANALYSIS STUDIES ON COMPLEXES OF COBALT(II), NICKEL(II), AND COPPER(II) WITH 3-PICOLYLAMINE

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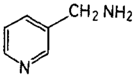
Some complexes of the thiocyanates, chlorides and bromides of cobalt(II), nickel(II) and copper(II) with 3-picolylamine have been prepared. The stereochemical configurations of the complexes were deduced using spectral and magnetic properties. The decomposition of the complexes was studied by thermogravimetry and differential thermal analysis.

This work is a continuation of previously reported studies [1–4] on the coordination compounds formed between the first row transition metals and the substituted pyridines.

This paper describes the preparation of complexes formed by the thiocyanates, chlorides and bromides of cobalt(II), nickel(II) and copper(II) with 3-picolylamine along with thermal analyses and spectroscopic and magnetic investigations of the products.



The 3-picolylamine possesses two potential donor sites; the pyridine ring nitrogen and the amino group and can thus act as a unidentate or bidentate ligand.

Experimental

The following three methods of preparation were used:

(A) A solution of about 3 g of metal halide in 30 cm^3 ethanol was obtained by warming until the ethanol boiled. To this boiling solution, 10 cm^3 of 3-picolylamine was added slowly, with stirring. The precipitated complexes were filtered, washed with ethanol and dried over calcium chloride.

(B) A complex prepared by method (A) was heated on a thermal balance in static air, at a fixed temperature, until constant weight was obtained. The fixed

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temperature was chosen between the initial temperature T_i and the final temperature T_f for that stage of the reaction.

(C) The thiocyanate complexes were prepared by the addition of potassium thiocyanate (0.02 M) in ethanol to the nitrates of the metal (0.01 M) in ethanol. The precipitate obtained was filtered off and 3-picolylamine was added to the thiocyanate solution, with stirring, until precipitation of the complex was complete. The precipitated complexes were filtered, washed with ethanol and dried over calcium chloride.

The complexes prepared by these methods are listed in Table 1 and are considered to be new compounds. Thermal decomposition studies (Table 2, Figs 1–3) were carried out using a Stanton Redcroft Model STA 781 working at a

Table 1 Analyses of complexes

Compound	Colour	% Metal		% Anion		Method of preparation
		theory	expt.	theory	expt.	
$Co(CNS)_2(3\text{-pa})_2$	Pink	15.10	14.82	29.70	29.10	C
$CoCl_2(3\text{-pa})_2$	Pink	17.05	16.90	20.52	20.62	A
$Co_3Cl_6(3\text{-pa})_4$	Purple	21.38	21.10	25.88	25.38	B
$CoBr_2(3\text{-pa})_2$	Pink	13.56	13.34	36.78	36.44	A
$Ni(CNS)_2(3\text{-pa})_2$	Violet	15.00	14.72	29.70	29.46	C
$NiCl_2(3\text{-pa})_4$	Blue	10.50	10.80	12.50	12.60	A
$Ni_3Cl_6(3\text{-pa})_2$	Yellow	29.10	28.72	35.21	34.86	B
$NiBr_2(3\text{-pa})_2$	Blue	13.50	13.60	36.80	36.90	A
$NiBr_2(3\text{-pa})$	Yellow	17.97	17.62	48.98	48.50	B
$CuCl_2(3\text{-pa})_2$	Blue	18.20	17.82	19.40	19.60	A
$CuBr_2(3\text{-pa})_2$	Green	14.50	14.50	35.80	35.90	A

Table 2 Thermal decomposition products
Compounds for which intermediates were isolated

Starting material	Decomposition temperature, K	% Mass loss		Resulting compound
		calculated	observed	
$CoCl_2(3\text{-pa})_2$	406 (ENDO)	20.81	20.81	$Co_3Cl_6(3\text{-pa})_4$
	663 (EXO)	83.14	81.37	Co_3O_4
$NiCl_2(3\text{-pa})_4$	324 (ENDO)	63.19	62.73	$Ni_3Cl_6(3\text{-pa})_2$
	480 (ENDO)	75.69	74.77	$NiCl_2$
	578 (EXO)	88.31	89.35	NiO
$NiBr_2(3\text{-pa})_2$	370 (ENDO)	24.21	24.11	$NiBr_2(3\text{-pa})$
	751 (EXO)	86.90	85.01	NiO

* The temperatures quoted are the initial temperature, T_i

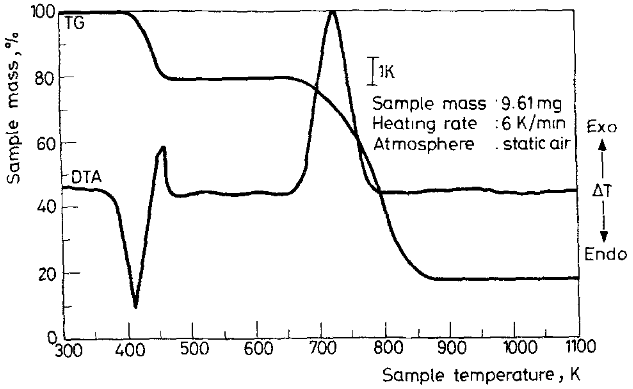

Fig. 1 Simultaneous TG/DTA curve for $CoCl_2(3\text{-pa})_2$

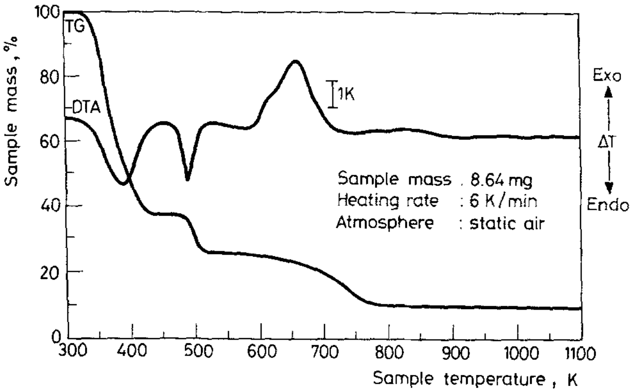

Fig. 2 Simultaneous TG/DTA curve for $NiCl_2(3\text{-pa})_4$

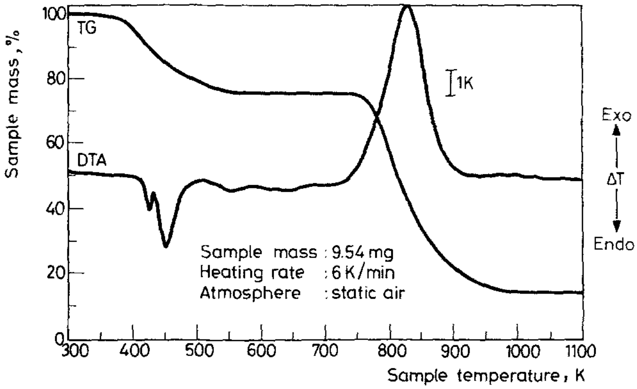

Fig. 3 Simultaneous TG/DTA curve for $NiBr_2(3\text{-pa})_2$

Table 3 Magnetic moments of the prepared complexes

Compound	Temp., K	χ_L $m^3mol^{-1}\cdot10^{-12}$	χ_M^{CORR} $m^3mol^{-1}\cdot10^{-9}$	μ_B, $Am^2\cdot10^{-23}$
$Co(CNS)_2(3\text{-pa})_2$	282	2578.37	0.14200	4.7014
$CoCl_2(3\text{-pa})_2$	298	3257.20	0.14577	4.8961
$CoBr_2(3\text{-pa})_2$	292	3660.83	0.14941	4.9054
$Ni(CNS)_2(3\text{-pa})_2$	282	2578.37	0.05316	2.8746
$NiCl_2(3\text{-pa})_4$	282	4038.33	0.05605	2.9488
$NiBr_2(3\text{-pa})_2$	295	3660.83	0.05341	2.9488
$CuCl_2(3\text{-pa})_2$	298	3257.20	0.01709	1.6784
$CuBr_2(3\text{-pa})_2$	282	3660.83	0.01294	1.4187

Table 4 Important infrared bands for the prepared complexes, cm^{-1}

Compound	$\nu_{a(NH_2)}$	$\nu_{s(NH_2)}$	$S(NH_2)$	Ring vibrations		$\nu_{(M-N)}$		$\nu_{(M-X)}$
3-pa	3350	3260	1623	1588	1475			
$Co(CNS)_2(3\text{-pa})_2$	3268	3239	1600	1590	1478	400	347	—
$CoCl_2(3\text{-pa})_2$	3310	3265	1595	1590	1475	382	340	292
$CoBr_2(3\text{-pa})_2$	3308	3262	1595	1588	1475	380	340	236
$Ni(CNS)_2(3\text{-pa})_2$	3280	3240	1600	1590	1479	410	349	—
$NiCl_2(3\text{-pa})_4$	3295	3250	1595	1590	1475	390	350	300
$NiBr_2(3\text{-pa})_2$	3290	3240	1600	1590	1472	392	360	226
$CuCl_2(3\text{-pa})_2$	3300	3280	1600	1590	1478	399	343	286
$CuBr_2(3\text{-pa})_2$	3295	3260	1603	1582	1478	395	345	220

chart speed of 200 mm/h and a heating rate of 6°/min. In some cases the complexes decomposed in a stepwise fashion with the formation of definite intermediate compounds. Flat positions in the pyrolysis curves bear evidence to their existence. The samples were ground in an agate mortar and pestle and placed in a Rhodium/Platinum crucible (diameter 5.8 mm; height 4 mm), the monitoring thermocouple being below the crucible. The reference compound used was ground alumina. The TG/DTA curves (Figs 1–3) are not a direct copy of those obtained from the instrument: the temperatures quoted have been obtained from a chart provided by the manufacturer.

The electronic spectra (Table 5) were obtained on a Beckmann ACTA M–IV spectrophotometer using DMSO as a solvent for the copper complexes and as solid diffuse reflectance spectra for the cobalt and nickel complexes.

The magnetic susceptibility measurements were made by the Gouy Method using a Newport Variable Temperature Balance and with $Hg[Co(SCN)_4]$ as calibrant.

The complexes were studied over the temperature range 300–100 K and the results fitted to the Curie–Weiss equation.

$$\mu = 2.84[\chi_M^{CORR}(T+\theta)]^{\frac{1}{2}}$$

Diamagnetic corrections were applied using the atomic diamagnetic susceptibilities tabulated by Figgis and Lewis [5].

Table 5 Electronic spectral details of the prepared complexes

Compound	Peak positions, cm^{-1}	Dq	Conc., mol dm^{-3}	ε, $m^2 mol^{-1}$
$Co(CNS)_2(3\text{-pa})_2$[a]	$\nu_1 = 7692$ $\nu_3 = 18348$	874	—	—
$CoCl_2(3\text{-pa})_2$[a]	$\nu_1 = 9615$ $\nu_3 = 19602$	1069	—	—
$CoBr_2(3\text{-pa})_2$[a]	$\nu_1 = 10416$ $\nu_3 = 19608$	1156	—	—
$Ni(CNS)_2(3\text{-pa})_2$[a]	$\nu_1 = 10640$ $\nu_2 = 17240$ $\nu_3 = 27030$	1064	—	—
$NiCl_2(3\text{-pa})_4$[a]	$\nu_1 = 9434$ $\nu_2 = 16010$ $\nu_3 = 26310$	943	—	—
$NiBr_2(3\text{-pa})_2$[a]	$\nu_1 = 8196$ $\nu_2 = 16000$ $\nu_3 = 25640$	819	—	—
$CuCl_2(3\text{-pa})_2$[b]	$\nu_1 = 12284$	—	2.637×10^{-3}	1.25
$CuBr_2(3\text{-pa})_2$[b]	$\nu_1 = 12498$	—	1.957×10^{-3}	1.31

[a] — Reflectance spectra

[b] — Solution spectra

The infrared spectra (Table 4) using KBr discs, 2000–600 cm^{-1}, and polyethylene discs, 600–200 cm^{-1}, were obtained with a Perkin–Elmer Infrared Spectrophotometer Model 598. 1 g of the complex and 3 g of KBr or polymer were ground in an agate pestle and mortar.

The analyses of the transition metal ions were determined by a Perkin–Elmer 373 atomic absorption spectrophotometer; the thiocyanate ion using mercury(II) nitrate [6a]; the chloride and bromide ions using Volhards method [6b].

Results and discussion

The complexes prepared, their analyses and method of preparation are listed in Table 1. The results of the thermogravimetric studies are given in Figs 1–3 and Table 2. The cobalt complexes have stoichiometry $Co(CNS)_2(3\text{-pa})_2$, $CoCl_2(3\text{-pa})_2$ and $CoBr_2(3\text{-pa})_2$. Thermal decomposition studies show that the thiocyanate complex has no intermediate decomposition steps but undergoes an endothermic reaction at 454 K, followed by an exothermic reaction at 663 K with loss of organic ligand and the thiocyanate to give Co_3O_4, as a result of concomitant aerial oxidation. The chloro complex (Fig. 1) undergoes an endothermic reaction at 406 K with loss of two-thirds of a molecule of 3-picolylamine, followed by an exothermic reaction at 663 K with loss of the remaining 3-picolylamine and the chlorine to give Co_3O_4. The bromo complex undergoes an endothermic reaction at 418 K followed by an exothermic reaction at 646 K with loss of the 3-picolylamine and bromine and the formation of Co_3O_4. The electronic spectra of the complexes are typical of the cobalt(II) ion in an octahedral environment [1] and have $Dq > 440\ cm^{-1}$ [4]. The magnetic data for the compounds (Table 3) agree with the suggestion of an octahedral arrangement of ligands around the cobalt ion with temperature dependent magnetic moments in the range 4.9–5.2 BM [4]. The compounds obey the Curie–Weiss law with positive values of θ.

The nickel complexes have stoichiometry $Ni(CNS)_2(3\text{-pa})_2$, $NiCl_2(3\text{-pa})_4$ and $NiBr_2(3\text{-pa})_2$. Thermal decomposition studies show that the thiocyanate complex has no intermediate decomposition products, but undergoes an endothermic reaction at 400 K, followed by an exothermic reaction at 672 K with loss of the 3-picolylamine and the thiocyanate to give NiO. The chloro complex (Fig. 2) undergoes two endothermic reactions, at 324 K and 480 K, followed by an exothermic reaction at 578 K, with loss of three and a third molecules of 3-picolylamine, a further two-thirds molecule of 3-picolylamine and chlorine respectively with the formation of NiO. The bromo complex (Fig. 3) undergoes an endothermic reaction at 370 K with loss of one molecule of 3-picolylamine and an exothermic reaction at 751 K with loss of the remaining 3-picolylamine molecule and bromine. The electronic spectra of the complexes are similar to those normally observed for nickel(II) in an octahedral environment [2] with the expected values for 10 Dq [7]. This suggestion of an octahedral environment for the nickel atom is further supported by the fact that the compounds have temperature independent magnetic moments in the range 2.8–3.2 BM [2]. The complexes obey the Curie–Weiss law with positive values of θ.

The chloro and bromo complexes of copper have stoichiometry $CuX_2(3\text{-pa})_2$. The thiocyanate complex was found to be unstable. Thermal decomposition studies of the chloro and bromo complexes show that they undergo exothermic reactions at

454 K and 494 K respectively, each losing 3-picolylamine and the halogen. The electronic spectra of the chloro and bromo complexes show bands at 12,284 cm^{-1} and 12,498 cm^{-1} respectively. This suggests an octahedral environment for the copper atom since square planar copper(II) compounds show bands of near equal intensity in the region 15,000 cm^{-1}–18,000 cm^{-1} [8–10]. Furthermore the bands compare favourably with those previously reported at 12,905 and 12,610 cm^{-1} for octahedral copper(II) complexes of nicotinic acid [2]. The values for the extinction coefficients for the complexes also agree with an octahedral environment for the copper ion [11]. The broadness of the bands is due to Jahn Teller distortion which results from an odd number of electrons in the $d_{x^2-y^2}$ orbital [12]. The band is considered to be composite bands involving transitions from the other *d*-orbitals to the $d_{x^2-y^2}$ orbital. The magnetic moments of the complexes which are independent of temperature are lower than those expected for the spin only value normally observed for octahedral copper(II) complexes. It is suggested that this is due to some copper-copper magnetic interaction in the complexes [13]. The complexes obey the Curie–Weiss law with positive values of θ.

The important bands in the infrared spectra of the complexes are listed in Table 4. A comparison of the bands of the infrared spectra of the complexes with that of the organic ligand shows that the spectra are similar in the region 2000–650 cm^{-1}. The ring vibrations of the 3-picolylamine show little change on coordination. In the region 3100–3500 cm^{-1} the $\nu_s(N-H)$ and $\nu_a(N-H)$ vibrations move to lower frequency. These observations suggest coordination through the nitrogen of the amine group of the 3-picolylamine [14].

Without X-ray analysis, no definite structures can be described. However spectroscopic and magnetic data enable us to predict possible structures. Dichlorotetrakis(3-picolylamine)nickel(II) has an octahedral structure with the 3-picolylamine being attached to the nickel atom through the nitrogen atom of the amine group. The MX_2L_2 compounds have octahedral structures. The poor solubility of the compounds in both polar and non-polar solvents together with bands at 280–300 cm^{-1} in the chloro compounds [15], at 220–240 cm^{-1} in the bromo compounds [3] and at 2140 cm^{-1} in the thiocyanate complexes [16] would suggest the presence of bridging halogen and thiocyanate groups. It is therefore suggested that the structure consists of a polymeric chain of $M-X$ atoms with organic ligands bonded both above and below the plane of the chain to each metal atom through a lone pair of electrons of the amine group of the 3-picolylamine.

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Zusammenfassung — Einige Komplexe der Thiocyanate, Chloride und Bromide von Kobalt(II) und Kupfer(II) mit 3-Picolylamin wurden hergestellt. Die stereochemischen Konfigurationen der Komplexe wurden aus den spektralen und magnetischen Eigenschaften abgeleitet. Die Zersetzung der Komplexe wurde thermogravimetrisch und differentialthermoanalytisch untersucht.

Резюме — Получен ряд комплексов тиоцианатов, хлоридов и бромидов двухвалентных кобальта, никеля и меди с 3-пиколиламином. Термическое разложение комплексов изучено методом ТГ и ДТА. Стереохимия комплексов установлена на основе их спектральных и магнитных свойств.