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THERMAL STABILITY OF BIS-PIPERIDINE BENZOYLACETONATES OF SOME TRANSITION METALS

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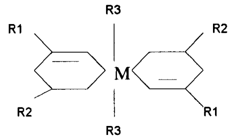
Abstract

Bis-piperidine complexes of benzoylacetonates of Mn(II), Co(II), Cd(II) and Ni(II) were prepared. Thermogravimetric analysis (TG) demonstrated that Mn(II) bis-piperidine benzoylacetonate was stable up to 90°C, while Co(II) bis-piperidine benzoylacetonate was stable up to 100°C, whereas Cd(II) bis-piperidine benzoylacetonate was stable up to only 50°C. Its first decomposition step was completed at 110°C. Ni(II) bis-piperidine benzoylacetonate found to be stable up to 110°C. The stabilities of the complexes of these metals therefore follow the sequence $Cd^{2+}<Mn^{2+}<Co^{2+}<Ni^{2+}$. The complex of Cd(II) was the least stable of all the compounds studied.

Keywords: bis-piperidine benzoylacetonate, thermal stability, transition metals

Introduction

The chelated compounds of a metal with bis-piperidine benzoylacetonate ($M(II)C_{30}H_{38}O_4N_2$) may be represented in the following form:
where *M*= metal, $R1=CH_3$, $R2=C_6H_5$ and $R3=C_5H_{10}N$. Piperidine is an analog of cyclohexane, in which one of the CH_2 units is replaced by NH. The charge resonance structure and dipole moment show that the piperidine ring has surplus negative charge on the nitrogen. Thus, piperidine is a strong field ligand and it forms inner *d*-orbital complexes.



Numerous studies have been reported on the thermal decompositions of metal complexes of 1,3-β-diketones. Some of the most useful studies are to be found in references [1–7]. Many of these metallic derivatives decomposes on strong heating, and it is of interest to find a 1,3-β-diketone that will give more stable derivatives.

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The aim of this work is to prepare bis-piperidine benzoylacetonate of Mn(II), Co(II), Cd(II) and Ni(II) and to study their structures by using X-ray diffraction and their thermal decompositions by using thermogravimetric techniques.

Experimental

A stoichiometric method of preparation of the bis-piperidine complexes of BACs [benzoylacetonate abbreviated as BAC] of Mn(II), Co(II), Cd(II) and Ni(II) was adopted. In this method, a 1:2 ratio by mass of metal and ligand was taken. The BACs of the metals were prepared first. For this purpose, the calculated amounts of $MnSO_4{\cdot}H_2O$, $CoCl_2{\cdot}6H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$ and $NiCl_2{\cdot}6H_2O$ were dissolved in 50 ml of distilled water in separate beakers. A solution of benzoylacetone (1 g in 15 ml of methanol) was prepared for each of the salt solutions. The two solutions were mixed together. Concentrated ammonia was added dropwise until a precipitate was formed. This was filtered through a Buckner funnel, washed with deionized water and dried. After crystallization from its solution in methanol, crystals of M(II)BAC (where M= Mn, Co, Cd, Ni) were obtained. In the next step, bis-piperidine complexes of M(II)BAC were obtained by dissolving 2 g of M(II)BAC in 30 ml of methanol and then adding in it a solution of 3.0 ml of piperidine in 15 ml of methanol. The two solutions were mixed and refluxed for 1 h. The dried products were recrystallized from methanol. The yields and melting points of the complexes were noted.

The metal contents were estimated by atomic absorption spectroscopy. For this purpose, known amounts of the bis-piperidine complexes of the metal BACs were added to 20 ml of 6 mol l^{-1} HCl. This led to decomposition of the complexes. This process was repeated 3–4 times. The residue was dissolved in 100 ml of distilled water. The metal chloride was formed in solution and benzoylacetone was filtered off. Standard solutions were prepared from 1 g of metal granules dissolved in 20 ml of 6 mol l^{-1} HNO_3. The solutions were diluted up to the desired mark with deionized water.

Results

X-ray powder diffraction results concerning the crystal class and the lattice parameters of these compounds are listed in Table 1. The standard JCPDS powder diffraction files do not contain listings of the bis-piperidine metal complexes of BAC, and confirmation of our results was therefore not possible. However, the criterion of de Wolff [8] for the reliability of the indexing was used. A figure of merit $M\geq10$ indicates that the indexing is satisfactory. The de Wolff figure of merit of each complex is given in Table 1.

The metal contents determined in the bis-piperidine metal BACs were Mn 10.061% (calcd. 10.076%), Co 6.85% (calcd. 6.9%), Cd 38.51% (calcd. 38.3%) and Ni 4.54% (calcd. 4.42%).

TG/DTA curves of bis-piperidine Mn(II)BAC are shown in Fig. 1. Mn(II)BAC loses 6.83% of the total mass in the form of the trimethyl ether $C_{20}H_{18}O$ while de-

Table 1 Lattice parameters of bis-piperidine benzoylacetonates (BACs) of Mn(II), Co(II), Cd(II) and Ni(II)

Complex	Lattice parameter							
	a/Ĺ	b/Ĺ	c/Ĺ	Volume of unit cell/Ĺ^3	α/°	β/°	γ/°	de Wolff factor of merit*
bis-piperidine Mn(II)BAC	8.2268	18.2137	11.7210	1389.6	140.3	95.8	94.3	$M_{20} = 16.2$
bis-piperidine Co(II)BAC	8.6437	12.2828	10.3994	972.49	110.63	104.6	97	$M_{16} = 10.7$
bis-piperidine Cd(II)BAC	8.9184	12.9292	7.9034	853.98	97	99	105.6	$M_{24} = 17$
bis-piperidine Ni(II)BAC	7.4153	17.5165	10.4033	1115.0				$M_{18} = 13.6$

* see Ref. [8] for explanation

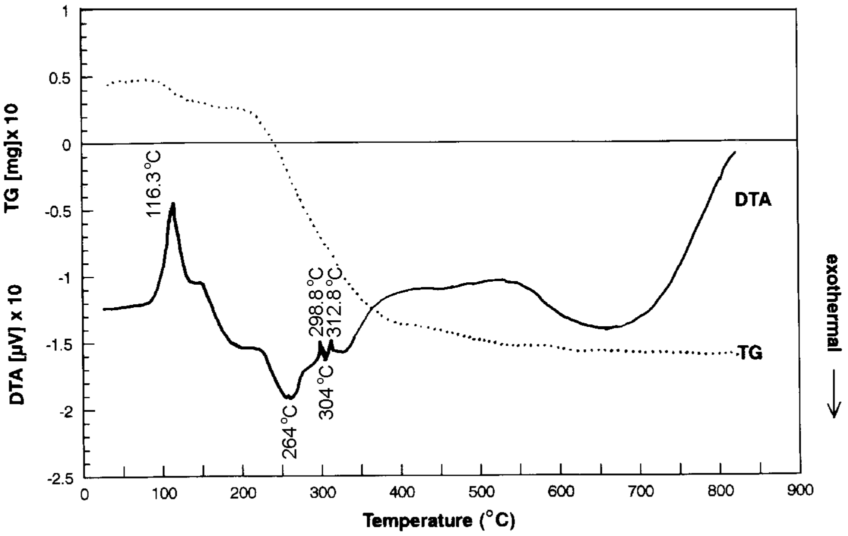

Fig. 1 TG/DTA curves of bis-piperidine Mn(II) benzoylacetonate

composing between 90 and 115°C. The next decomposition takes place in the interval 220–460°C, with a loss of 54.04% in mass in the form of (*E*)-N,N-dimethyl-2-propenylamine, $C_5H_{11}N$. The residue remains stable up to 840°C. Final decomposition takes place between 840 and 1020°C, giving 18.39% of MnO.

The TG/DTA curves of bis-piperidine Co(II)BAC indicated that the complex is stable up to 100°C, and it loses 74.34% of the total mass between 100 and 520°C.

The TG/DTA curves of bis-piperidine Cd(II)BAC showed that the complex is stable up to 50°C; it loses 13.7% of the total mass between 50 and 100°C. In this step, one piperidine molecule is lost. In the next step, 48.49% of the total mass is lost due to the elimination of one BAC group and one acetyl group between 110 and 420°C. In the last step, between 420 and 700°C, 17.05% of the total mass is lost in the form of phenylacetylene. The residue of CdO is stable after 700°C.

The TG/DTA curves of bis-piperidine Ni(II)BAC indicated that the complex is stable up to 110°C. It decomposes between 110 and 240°C, losing 16.43% of the total mass, which may be piperidine. In the next step, the residue decomposes between 240 and 460°C, losing 49.06% of the total mass: another molecule of piperidine, a benzoyl group and allylene oxide. In the third step, decomposition between 460 and 550°C results in the loss of 6.31% of the total mass, a C_2H_3O (acetyl group) being eliminated.

The TG results on the four bis-piperidine compounds are compared in Table 2. It may be noted that bis-piperidine Cd(II)BAC has the lowest initial decomposition temperature (50°C), while bis-piperidine Ni(II)BAC has the highest first-stage decomposition temperature (110°C).

It is well known that transition element cations readily form chelate compounds, i.e. they have low-lying vacant orbitals which are capable of accepting electron pairs to form homopolar bonds. Manganese, cobalt and nickel have electron configurations of (Ar core) 3d^{x}4s^2, where x=5, 7 and 8, and Cd^{2+} has the configuration (Kr core) 4d^{10}5s^2. The forces holding the metal ions in the compounds are ionic or coulombic in nature, involving the effects of charge, the charge distribution of the anion and the ionic radius. The stabilities of the bis-piperidine BACs of the four transition metals (having ionic radii Cd^{2+}=0.96 Ĺ, Mn^{2+}=0.8 Ĺ, Co^{2+}=0.72 Ĺ, Ni^{2+}=0.69 Ĺ) follow the series Cd^{2+}<Mn^{2+}<Co^{2+}<Ni^{2+}. It is well known that, as the ionic radius decreases, the polarizing power of the ion increases, resulting in an increase in stability of the bonding between the metal ion and the ligand. Cadmium happens to be at the end of the second transition series and its *d* orbitals project further into space towards the ligands, so that the electrostatic repulsion between the ligands and the *d* electrons is increased, resulting in a decrease in stability.

Table 2 TG results on bis-piperidine benzoylacetonates (BACs) of Mn(II), Co(II), Cd(II) and Ni(II)

Compound	Temperature/°C	Total mass loss/%	Nature
bis-piperidine	0–90		stable
Mn(II)BAC	90–115	6.83	decomposition
	220–460	54.05	decomposition
	840–1020	18.39	decomposition
bis-piperidine	0–100		stable
Co(II)BAC	100–520	74.34	decomposition
bis-piperidine	0–50		stable
Cd(II)BAC	50–110	13.27	decomposition
	110–420	48.49	decomposition
	420–700	17.05	decomposition
bis-piperidine	0–110		stable
Ni(II)BAC	110–240	16.43	decomposition
	240–460	49.06	decomposition
	460–550	6.31	decomposition

The stability of a complex can be explained in terms of its molar volume. Table 1 shows the volume of the unit cell of each complex. The molar volume of a complex can be determined from the volume of the unit cell and the number of formula units (Z) it contains. The latter is found to be equal to 2 for all the complexes studied in this work. If the molar volume of a complex is large, the interactions between the chelating ligands and the metal atoms are small. Thus, Ni(II) bis-piperidine BAC is the most stable of these chelates as its molar volume is the largest of those for the four complexes.

Conclusions

The stabilities of four chelate compounds (bis-piperidine BACs of the first and second transition series) have been studied on the basis of thermogravimetric analysis. The compounds display initial decomposition temperatures in the sequence $Cd^{2+}<Mn^{2+}<Co^{2+}<Ni^{2+}$. Cadmium happens to be at the end of the second transition series, and the Cd^{2+} chelate is the least stable of all the compounds studied in this work.

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