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ANIONIC 2,6-PYRIDINEDICARBOXYLATE COMPLEXES WITH SOME DIVALENT FIRST-ROW TRANSITION METALS

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Abstract—A series of $Na_2[M(pdc)_2]\cdot nH_2O$ complexes ($M = Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}$, and Zn^{II}; pdc^{2-} = pyridine-2,6-dicarboxylate; $n = 2$ or 3) have been synthesized and characterized via molar conductance, magnetic susceptibility, IR and electronic spectral measurements, and thermogravimetry. The compounds are 2 : 1 electrolytes in aqueous solution and contain six-coordinate anionic complex ions. The loss of water and the decomposition of the anhydrous salts differ from compound to compound in this series; residues consist of Na_2CO_3 and metal oxide.

Pyridine-2,6-dicarboxylic acid (also known as dipicolinic acid and abbreviated herein as H_2pdc) has been studied extensively as a Lewis base. The interest in this ligand seems to centre on the versatile yet unpredictable manner in which it coordinates to a variety of metals. For example, X-ray studies have shown that complexes such as $Ag(Hpdc)_2\cdot H_2O$[1] and $Cu(Hpdc)_2\cdot 3H_2O$[2] actually contain one neutral H_2pdc and one pdc^{2-} ligand, while $Ni(Hpdc)_2\cdot 3H_2O$[3–5] has two $Hpdc^-$ ligands. In contrast to the tridentate coordination of the ligands in the above complexes, $Hpdc^-$ is bidentate in $V(Hpdc)_3\cdot 3H_2O$.[6] Other types of complexes which have been reported, include some polymeric $M(pdc)\cdot nH_2O$ species ($M = Co^{II}, Ni^{II}, Cu^{II}$; $n = 0$, 2, or 3),[7–9] some mixed-ligand complexes with acetylacetonate, 1,10-phenanthroline, 2,2′-bipyridyl, or 2,2′,2″-terpyridyl,[9] a series of $M_2(pdc)(Hpdc)_2\cdot nH_2O$ complexes ($M = Co^{II}, Ni^{II}, Cu^{II}$; $n = 0$ or 2),[9] and a series of lanthanide complexes of the types $M(Hpdc)_3\cdot H_2O$ and $M(pdc)(Hpdc)(H_2O)_n$ ($n = 4$ or 6).[10,11]

Based upon the coordination number of six, commonly adopted by many transition metals, and the ability of pdc^{2-} to function as a tridentate ligand, one expects to find anionic complexes of the type $[M(pdc)_2]^{x-}$ ($x = 1$ or 2). A number of such complexes has been reported for trivalent metal ions, examples being $Na[M(pdc)_2]\cdot 2H_2O$ ($M = Ru^{III}$, Ir^{III}),[12] $Na[Cr(pdc)_2]\cdot 1.5H_2O$,[13] $Rh[Cr(pdc)_2]$[14] and some Nd^{III} and Yb^{III} complexes of the type $Na_3[M(pdc)_3]\cdot nH_2O$.[15] Apparently similar anionic complexes with divalent metal ions have not been studied. This work focuses on the series $Na_2[M(pdc)_2]$ where $M = Mn^{II}$, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}. Other anionic complexes previously reported included $(Ph_4As)_2[U(pdc)_3]\cdot 3H_2O$[16] and $(Ph_4As)_2[UO_2(pdc)_2]\cdot 6H_2O$.[17]

RESULTS AND DISCUSSION

Reaction of divalent metal carbonates and/or hydroxides with H_2pdc in aqueous solution in 1 : 1 or 1 : 2 mole ratios leads to $M(pdc)\cdot nH_2O$ and $M(Hpdc)_2\cdot nH_2O$, respectively,[2,7,8,18] with $M = Co^{II}$, Ni^{II} and Cu^{II}, and $n = 0$, 2, or 3. In this work, anionic complexes were prepared in aqueous solution by the reaction of divalent (hydrated) metal acetates, H_2pdc and NaOH in a 1 : 2 : 2 mole ratio. Elemental analyses and thermogravimetric data confirm the stoichiometry of the complexes as $Na_2[M(pdc)_2]\cdot nH_2O$ where $M = Mn^{II}$ and Co^{II} with $n = 2$, and where $M = Ni^{II}$, Cu^{II} and Zn^{II} with $n = 3$. Conductance measurements on 0.001 M aqueous solutions (Table 1) indicate the presence of 2 : 1 electrolytes, for which Λ_M is expected to be in the 230–270 $cm^2\ ohm^{-1}\ mol^{-1}$ range.[19] While the reason for the slightly low values for the Ni^{II} and Cu^{II} complexes is unknown, the behaviour is similar to that observed for the Rh^{III} and Ir^{III}

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Na[M(pdc)$_2$] complexes, where Λ_M values in DMF fell essentially into the non-electrolyte range.[12]

IR data on the solid Na$_2$[M(pdc)$_2$]$\cdot n$H$_2$O compounds are consistent with coordination of pdc^{2-}. The $\bar{\nu}_{sym}$(COO) band is shifted as expected from the free ligand value of 1290 cm^{-1} into the range 1376–1360 cm^{-1}. Similarly, the $\bar{\nu}_{asym}$(COO) band is shifted from the free ligand value of 1658 cm^{-1} into the range 1629–1613 cm^{-1}, and no bands appear near 1700 cm^{-1} as was the case when Hpdc$^-$ or H$_2$pdc was also present, such as in complexes of the type M$_2$(pdc)(Hpdc)$_2$.[9] The shift, $\Delta\bar{\nu}_{asym}$(COO), of about 40 cm^{-1} is consistent with the absence of an extended interaction in which the $>$C=O group of one ligand interacts with a second metal centre.[12] In addition, the extremely broad band in the 3200–2400 cm^{-1} range due to hydrogen-bonded —COOH groups in H$_2$pdc is absent in the complexes, further confirming complete deprotonation of H$_2$pdc. The typical upward shift of major pyridine ring bands is indicative of coordination of the ring nitrogen. A broad band centred at about 3390 cm^{-1} appears in the spectrum of the Ni^{II} and Cu^{II} complexes, due to the presence of the water of hydration. The Mn^{II}, Co^{II} and Zn^{II} complexes show a similar broad band centred around 3200 cm^{-1}, but each displays an additional sharp shoulder at 3534 cm^{-1}.

A coordination number of six suggests a pseudo-octahedral coordination sphere about the metal ions. Room temperature magnetic data (Table 1) are consistent with high-spin six-coordinate M(pdc)$_2^{2-}$ species. The observed magnetic moments are similar to those of M(Hpdc)$_2\cdot$3H$_2$O, M(pdc)$\cdot$3H$_2$O, M(pdc) and M$_2$(pdc)(Hpdc)$_2\cdot n$H$_2$O ($n = 0$ or 2) species: 5.25–4.54 μ_B for Co^{II}; 3.45–2.85 μ_B for Ni^{II}, and 1.93 μ_B for the latter Cu^{II} complex.[7,9]

Electronic absorption spectra of the Na$_2$[M(pdc)$_2$]$\cdot n$H$_2$O complexes are summarized in Table 1. The Cu^{II} complex has the single band expected for a six-coordinate d^9 species. Spectra of the Ni^{II} and Co^{II} complexes are also typical of six-coordinate species; most of the absorption peaks have clearly defined shoulders which suggest distortion from octahedral symmetry. The spectra of the latter two complexes are very similar to those reported for the corresponding Ni^{II} and Co^{II} M(Hpdc)$_2\cdot$3H$_2$O complexes.[7]

Several pdc^{2-} and Hpdc$^-$ complexes have been studied via thermogravimetric analysis. The thermogram of (Ph$_4$As)$_2$[UO$_2$(pdc)$_2$]$\cdot$6H$_2$O showed that water was lost up to about 120°C in three steps (first one, then three, then two moles). The anhydrous salt then decomposed between 250 and 450°C in several steps, proceeding via an intermediate proposed to be UO$_2$(pdc-Ph)$_2$ after the loss of two moles of AsPh$_3$.[16] Thermograms of the series M(Hpdc)$_2\cdot n$H$_2$O (M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}; $n = 0$, 2, or 3) were reported by D'Ascenzo *et al.*[18] In air, the hydrates Co(Hpdc)$_2\cdot$3H$_2$O, Ni(Hpdc)$_2\cdot$3H$_2$O and Zn(Hpdc)$_2\cdot$2H$_2$O lost all their moles of water in a single step, while Fe(Hpdc)$_2\cdot$2H$_2$O lost its water in two steps. All anhydrous compounds decomposed in two steps yielding the oxides Mn$_3$O$_4$, Fe$_2$O$_3$, Co$_3$O$_4$, NiO, CuO and ZnO. The order of stability was found to be Mn > Fe > Zn > Co > Ni > Cu, the reverse of the Irving–Williams sequence.

For the Na$_2$[M(pdc)$_2$]$\cdot n$H$_2$O complexes studied here (Table 2 and Fig. 1), the three trihydrates (M = Zn^{II}, Ni^{II}, Cu^{II}) lose water in two steps (first two moles, then one mole). The dihydrates behave differently, with the Mn^{II} complex losing water in a single step and the Co^{II} complex losing it in two steps. There seems to be no correlation of the manner in which the water is lost and the appearance of the bands in the O—H stretching region of the aforementioned IR spectra. Decomposition of the anhydrous salts occurs in two distinct steps for Zn^{II}

Table 1. Conductance, magnetic and spectral data

Complex	Molar conductance[a] Λ_M (cm^2 ohm^{-1} mol^{-1})	Magnetic moment[b] μ_B	Electronic absorption spectra[c] λ (nm) [ε (dm^3 mol^{-1} cm^{-1})]
Na$_2$[Mn(pdc)$_2$]$\cdot$2H$_2$O	260	5.65	
Na$_2$[Co(pdc)$_2$]$\cdot$2H$_2$O	261	5.18	459[20], 489sh, 528sh; 580[20]; 947[7], 989[7]
Na$_2$[Ni(pdc)$_2$]$\cdot$3H$_2$O	221	3.25	363sh;[d] 616[10]; 923sh, 1021[32]
Na$_2$[Cu(pdc)$_2$]$\cdot$3H$_2$O	213	1.88	774[43]
Na$_2$[Zn(pdc)$_2$]$\cdot$3H$_2$O	232	diam.	

[a] 0.001 M in water.
[b] At 294 K.
[c] 0.014–0.022 M in water.
[d] Shoulder on charge-transfer band.

Table 2. Thermogravimetric data

Complex	Loss of water (%) calc. (found) $-H_2O$	$-2H_2O$	$-3H_2O$	Residue (%) Composition	calc. (found)
$Na_2[Mn(pdc)_2] \cdot 2H_2O$	3.86 —	7.71 (7.9)		$Na_2CO_3 + Mn_3O_4$	39.02 (38.9)
$Na_2[Co(pdc)_2] \cdot 2H_2O$	3.82 (4.4)	7.65 (7.5)		$Na_2CO_3 + Co_3O_4$	39.54 (39.4)
$Na_2[Ni(pdc)_2] \cdot 3H_2O$	3.68 —	7.37 (7.5)	11.05 (11.0)	$Na_2CO_3 + NiO$	36.96 (36.3)
$Na_2[Cu(pdc)_2] \cdot 3H_2O$	3.65 —	7.30 (7.4)	10.95 (10.7)	$Na_2CO_3 + CuO$	37.58 (37.0)
$Na_2[Zn(pdc)_2] \cdot 3H_2O$	3.64 —	7.27 (7.2)	10.91 (11.1)	$Na_2CO_3 + ZnO$	37.81 (37.3)

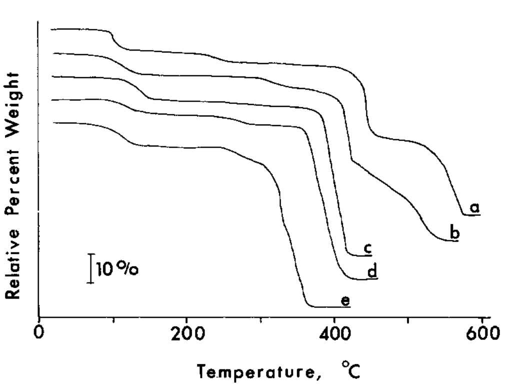

Fig. 1. Thermograms of $Na_2[M(pdc)_2] \cdot nH_2O$ complexes. (a) Zn, (b) Ni, (c) Mn, (d) Co, (e) Cu.

and Ni^{II}, in perhaps two overlapping steps for Cu^{II}, and apparently in a single step for Co^{II} and Mn^{II}. The order of stability is Zn > Ni > Mn > Co > Cu, with Ni being out of the position predicted by the reverse Irving–Williams sequence. The residues were identified based on total weight loss (Table 2) and by standard qualitative analysis tests to be mixtures of Na_2CO_3 and the respective oxides ZnO, CuO, NiO, Co_3O_4 and Mn_3O_4.

EXPERIMENTAL

Synthesis of $Na_2[M(pdc)_2]$ *complexes*

The ligand pyridine-2,6-dicarboxylic acid, sodium hydroxide and the hydrated metal acetate salts were AR-grade chemicals and were used without further purification.

Solid NaOH (20 mmol) was dissolved in 75 cm^3 of water and heated to near boiling in a 250 cm^3 round-bottom flask. The ligand H_2pdc (20 mmol) was added with stirring until solution was complete. The appropriate hydrated metal acetate (10 mmol), dissolved in 50 cm^3 of hot water, was added to the basic ligand solution and the mixture was refluxed for 1–2 h. The resulting solution was reduced in volume to less than 50 cm^3 by heating on a steam bath or using a rotary evaporator. Cooling in an ice bath induced crystallization of the crude product. Products were filtered, washed with *n*-butyl alcohol and dried in vacuum over P_2O_5. It was necessary to recrystallize the Ni^{II}, Cu^{II} and Zn^{II} complexes; each compound was dissolved in cold water, filtered to remove unreacted ligand, then evaporated to near dryness to recover the product, which was then washed and dried as described above. Yields were 85–95% for the Co^{II} and Mn^{II} complexes and 50–75% for the others.

Found: C, 35.9; H, 2.1; N, 5.8. Calc. for $Na_2Mn(C_7H_3NO_4)_2 \cdot 2H_2O$: C, 36.0; H, 2.2; N, 6.0%. Colour: yellow. Found: C, 35.6; H, 2.1; N, 5.8. Calc. for $Na_2Co(C_7H_3NO_4)_2 \cdot 2H_2O$: C, 35.7; H, 2.1; N, 5.9%. Colour: grey. Found: C, 35.0; H, 2.6; N, 5.9. Calc. for $Na_2Ni(C_7H_3NO_4)_2 \cdot 3H_2O$: C, 34.4; H, 2.5; N, 5.7%. Colour: green. Found: C, 34.8; H, 2.9; N, 5.7. Calc. for $Na_2Cu(C_7H_3NO_4)_2 \cdot 3H_2O$: C, 34.0; H, 2.4; N, 5.7%. Colour: blue. Found: C, 34.7; H, 2.5; N, 5.8. Calc. for $Na_2Zn(C_7H_3NO_4)_2 \cdot 3H_2O$: C, 33.9; H, 2.4; N, 5.6%. Colour: white.

Physical and spectral measurements

Magnetic susceptibility measurements were carried out on solid samples by the Gouy method at 294 K and 5400 G. $HgCo(SCN)_4$ was used as calibrant. Diamagnetic corrections were made using Pascal's constants. The temperature-independent paramagnetism correction of 60×10^{-6} cgsu was used for the Cu^{II} complex.

Molar conductance measurements were made on 0.001 M aqueous solutions using a Markson Electromark analyser. Potassium chloride solutions were used as standards.

IR spectra were obtained as KBr pellets in the range 4000–650 cm^{-1} on a Beckman IR-8 spectrophotometer. Electronic absorption spectra were obtained as aqueous solutions (0.014–0.022 M) in the range 1300–340 nm on a Cary 14 spectrophotometer.

Thermogravimetric measurements were made in air on a home-constructed apparatus utilizing an iron-constantan thermocouple, ice-bath reference and a heating rate of 6° min^{-1}.

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