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# Thermal and Electrical Properties of Transition Metal Complexes and Coordination Polymers of Pyrazine-2,5-dicarboxylic Acid

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*Complexes of copper, nickel, cobalt, palladium, and platinum with pyrazine-2,5-dicarboxylic acid have been prepared and characterized as potential semiconductors. All, however, showed power resistivities >10$^{12}$ ohm.*

## Introduction

There has been much recent interest in possible applications of organotransition metal complexes and coordination polymers in electrical devices, particularly semiconductors [1]. Of the transition metal complexes which have been examined for interesting electrical properties most have suffered from extremely low specific conductivities, low carrier mobilities, and high energy gaps. In the case of one-dimensional conductors of the type exemplified by the tetracyanoplatinates [2], these problems have been surmounted firstly by molecular structures which provide for through-conjugation of electrical carriers and secondly by the fact that the materials exist as single crystals with high degree of long-range order. There have been studies [1, 3] which indicate that planar organotransition metal coordination polymers formed with aromatic organic ligands might also possess molecular pathways for through-conjugation and be amenable to crystallization. For this reason we undertook a study of the thermal and bulk electrical properties of transition metal complexes and coordination polymers derived from the centrosymmetric, aromatic ligand pyrazine-2,5-dicarboxylic acid (PDCH$_2$) the tetradentate analogue of picolinic acid.

## Experimental

### Physical Measurements

Thermogravimetry was performed using an R. L. Stone TGA-5B Thermobalance (Cahn electrobalance) in a flowing nitrogen/oxygen atmosphere unless indicated. Samples ranging in size from 12 mg to 26 mg were run at a heating rate of 5 °C/min. Magnetic susceptibility measurements were made by the Gouy method using Hg[Co(NCS)$_4$] as calibrant. The hydrated cobalt and nickel PDC polymers were freshly dried and packed into the Gouy tube in a glove bag under dry nitrogen. IR spectra were taken on a Beckman IR8 spectrometer using KBr pellets. X-ray powder diffraction patterns were determined on a Hayes Powder Diffractometer using filtered Cu-Kα radiation (λ = 1.5418 Å). Conductivity measurements were taken with a Keithley 515 Megohm Bridge on powder samples pressed into the form of disks 1 cm in diameter and between 0.9 and 1.1 mm thick. Contact between bridge electrodes and sample disks was facilitated by spotting the disk with either Hg–In alloy or silver conducting paint. Resistance readings taken at ambient temperature in air or *in vacuo* were similar although resistances read in air slowly decreased as the sample adsorbed water vapor. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

### Preparations

#### Pyrazine-2,5-dicarboxylic acid

The ligand was prepared by the method of Schut, Mager, and Berends [4]. *Anal.*: Calcd. for $C_6H_4N_2O_4$, C 42.87, H 2.40, N 16.66; found: C, 42.75, H 2.26, N 16.60. The dimethyl ester melted at 167–168 °C (lit [4] 168–168.5 °C).

#### Hydrated PDC coordination polymers

The ligand PDCH$_2$ (0.01 mol) was dissolved in warm water by addition of 10% aqueous sodium hydroxide. An aqueous solution of metal salt (0.01 mol) was added and after several hours the precipitate was collected on a fritted glass funnel, washed well with water, and dried over $P_2O_5$ at 100 °C *in vacuo*. The brittle solids were ground to a powder before characterization. Metal salts used were $Cu(OAc)_2 \cdot H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, and $Co(NO_3)_2 \cdot 6H_2O$.

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TABLE I. Analyses of Complexes.

| Compound | Color | Calculated (%) | | | | Found (%) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | C | H | N | Metal | C | H | N | Metal |
| Cu•PDC | Dark Green | 31.37 | 0.87 | 12.19 | 27.68 | 31.11 | 1.08 | 12.13 | 27.44 |
| Ni•PDC•2½$H_2O$ | Lt. Green | 26.71 | 2.61 | 10.38 | 21.76 | 26.29 | 2.50 | 10.41 | 20.15 |
| Co•PDC•2$H_2O$ | Dark Yellow | 27.61 | 2.32 | 10.73 | 22.57 | 27.61 | 2.02 | 10.60 | 22.30 |
| Ni•PDC•2$NH_3$ | Yellowish Orange | 27.84 | 3.12 | 21.64 | 22.68 | 28.01 | 2.90 | 21.42 | 22.6[a] |
| Pd•PDC•2$NH_3$ | Yellow | 23.51 | 2.61 | 18.27 | 34.72 | 23.63 | 2.50 | 18.48 | 33.86 |
| Pd•PDC•4$NH_3$ | White | 21.16 | 4.14 | 24.67 | 31.24 | 21.16 | 4.20 | 24.61 | 31.2[a] |
| Pt•PDC•4$NH_3$ | White | 16.79 | 3.29 | 19.58 | 45.44 | 16.59 | 3.09 | 19.50 | 44.7[a] |

[a] Determined by TG.

TABLE II. IR Spectral Bands ($\nu$, $cm^{-1}$) and Magnetic Moments of Complexes.

| Compound | IR | $\mu_{eff}$ (B.M.) |
|---|---|---|
| Pd$CH_2$ | 3480m, 3000–2300b, 1705s, 1278s, 1173vs | |
| Cu•PDC | 3440b, 1655vs, 1382s, 1305s, 1178s, 840s | 1.87 |
| Ni•PDC•2½$H_2O$ | 3300b, 1650vs, 1388s, 1318s, 1185s, 840s | 3.12[a] |
| Co•PDC•2$H_2O$ | 3250b, 1650vs, 1388s, 1315s, 1183s, 835m | 4.52[a] |
| Ni•PDC•2$NH_3$ | 3350m, 3325m, 3260m, 1655vs, 1575m, 1378m, 1322s, 1215m, 1200m | 3.12 |
| Pd•PDC•2$NH_3$ | 3230m, 3095m, 3020m, 1695m, 1630vs, 1580m, 1390s, 1362m, 1320m, 1305s | Diamag. |
| Pd•PDC•4$NH_3$ | 3245s, 3150s, 1620vs, 1390s, 1302s, 827s | Diamag. |
| Pt•PDC•4$NH_3$ | 3250b, 1625vs, 1383s, 1302s, 815m | |

[a] Determined on anhydrous material.

*Ni•PDC•2$NH_3$*

The ligand (0.0046 mol) was dissolved in 250 ml water by addition of 5 ml aqueous ammonia. A solution of Ni$(NO_3)_2$•6$H_2O$ (0.0046 mol) in 50 ml water plus 25 ml aqueous ammonia was added and the solution was boiled for 1 hr. The precipitate was filtered and vacuum dried at 60 °C (20 mm). Yield was quantitative. Heating the compound in air for 4 hr at 190–220 °C produced Ni•PDC•2½$H_2O$ as shown by IR.

*Pd•PDC•2$NH_3$ and Pd•PDC•4$NH_3$*

The ligand (0.01 mol) was dissolved in 200 ml warm water by addition of 50% aqueous ammonia. A solution of Pd$Cl_2$ (0.01 mol) in 177 ml water plus 36 ml aqueous ammonia was added and the solution was boiled down to a volume of 200 ml. The Pd•PDC•2$NH_3$ was filtered, washed with ice water, and dried over $P_2O_5$ *in vacuo* at 100 °C. Yield was 87%. Boiling the material with aqueous ammonia yielded Pd•PDC•4$NH_3$ which was dried at room temperature over $P_2O_5$. Heating Pd•PDC•4$NH_3$ in water yielded Pd•PDC•2$NH_3$.

*Pt•PDC•4$NH_3$*

The ligand (0.0014 mol) and $K_2PtCl_4$ (0.0014 mol) were boiled with 130 ml 50% aqueous ammonia. Sufficient aqueous ammonia was added periodically to dissolve any white precipitate and to keep the solution from turning yellow. The solution was boiled down to 55 ml, cooled overnight, and the precipitate collected and dried *in vacuo* over $P_2O_5$ at 100 °C. Yield was 91%.

## Results and Discussion

Analytical data for all complexes are given in Table I. Non-ammoniated Cu, Ni, and Co•PDC polymers have been reported previously by Antinelli and Paris [5]. We have prepared these three materials in aqueous solution in the presence of base. The compounds were isolated as hydrates whose X-ray powder diffraction patterns consisted of several strong, diffuse bands along with lower intensity sharp bands indicative of only a low degree of crystallinity. The compounds did not melt but after loss of water decomposed around 300 °C by loss of the elements of $CO_2$ and pyrazine as shown by TG (Table III). Magnetic susceptibility measurements on dried Cu•PDC, Ni•PDC, and Co•PDC (Table II) were consistent with square planar geometry about the copper atom and octahedral geometry about the nickel and cobalt atoms. These respective geometries have

TABLE III. Results of Thermogravimetric Studies.

| Compound | Td (°C)[a] | Species Volatilized | Weight Loss (%) | | % Metal[b] |
|---|---|---|---|---|---|
| | | | Found | Calculated | |
| $PDCH_2$ | 240–310 | $C_4H_4N_2 + 2CO_2$ | 100 | 100 | |
| Cu•PDC | 50–125 | $(H_2O)$ | 2.5 | | |
| | 280–290 | $C_4H_4N_2 + 2CO_2$ | 65.6 | 72.3 | 27.5 (27.7CuO)[c] |
| Ni•PDC•2½$H_2O$ | 50–240 | 2½$H_2O$ | 17.2 | 16.7 | |
| | 310–315 | $C_4H_4N_2 + 2CO_2$ | 61.0 | 61.6 | 21.9 (21.8NiO)[c] |
| Co•PDC•$2H_2O$ | 50–235 | $2H_2O$ | 13.1 | 13.8 | |
| | 305–310 | $C_4H_4N_2 + 2CO_2$ | 61.9 | 63.6 | 22.5 (22.6$Co_3O_4$)[c] |
| Ni•PDC•$2NH_3$ | 240–295 | $2NH_3$ | 12.8 | 13.1 | |
| | 375–415 | $C_4H_4N_2 + CO_2 + CO$ | 58.8 | 58.0 | 22.2 (22.7NiO) |
| Pd•PDC•$2NH_3$[d] | 310–670 | $C_4H_4N_2 + 2CO_2 + 2NH_3$ | 65.0 | 65.3 | 35.0 (34.7Pd) |
| Pd•PDC•$4NH_3$[d] | 260–550 | $C_4H_4N_2 + 2CO_2 + 4NH_3$ | 68.8 | 68.7 | 31.2 (31.2Pd) |
| Pt•PDC•$4NH_3$[d] | 285–435 | $C_4H_4N_2 + 2CO_2 + 4NH_3$ | 55.3 | 54.6 | 44.7 (45.4Pt) |

[a] From first significant weight loss to beginning of plateau. [b] Calculated values in parenthesis with species weighed. [c] Observed weight gain at high temperature due to oxidation. [d] Nitrogen atmosphere.

already been shown for the corresponding picolinate [6] and similar [7] complexes. Magnetic susceptibilities and TG transition temperatures are in good agreement with those determined by Antinelli and Paris.

IR spectra for Cu•PDC, Ni•PDC•2½$H_2O$, and Co•PDC•$2H_2O$ (Table II) showed a strong carboxylate asymmetric stretch band between 1630 and 1665 $cm^{-1}$ as expected for a carboxylate group forming one covalent bond to a metal atom [8]. The three polymers also showed the requisite carboxylate symmetric stretch band at about 1315 $cm^{-1}$ although there is a somewhat weaker, unidentified band at about 1380 $cm^{-1}$.

To avoid complicating effects due to the presence of water during solid state conductivity measurements the three hydrated PDC polymers were dried before analysis and TG. The Cu polymer could be prepared anhydrous but the Ni and Co polymers were very hygroscopic. Powder resistivity of all three polymers was $>10^{12}$ ohm whether the material was hydrated or not. The compounds were quite intractable, being insoluble in a wide variety of polar solvents, and consequently studies on well-defined crystals were precluded.

PDC complexes with Ni, Pd, and Pt were also made in the presence of aqueous ammonia. Both Pd•PDC•$2NH_3$ and Pd•PDC•$4NH_3$ complexes could be isolated and the materials could be interconverted by heating in aqueous ammonia or water, respectively. Only the diammine Ni•PDC complex was observed and the compound was insoluble in hot aqueous ammonia. Heating Ni•PDC•$2NH_3$ in air gave Ni•PDC•2½$H_2O$. Only the tetraammine Pt•PDC complex was isolated and the compound was not labile in boiling water. X-ray powder diffraction patterns showed all four ammoniated PDC complexes to be crystalline. Pd•PDC•$4NH_3$ was isomorphous with Pt•PDC•$4NH_3$ but there was no similarity in the diffraction patterns of Pd•PDC•$2NH_3$ and Ni•PDC•$2NH_3$. Single crystal X-ray structure determination [9] on Pd•PDC•$4NH_3$ showed the molecular structure to consist of stacks of tetraammine palladium units with Pd–Pd distance of 3.77 Å. There was no bonding between Pd and the PDC ligand and the structure is reminiscent of the tetracyanoplatinates. Crystals of the tetraammine Pd and Pt•PDC complexes large enough for single crystal conductivity measurements could not be grown. Nevertheless, the Pd–Pd distance in Pd•PDC•$4NH_3$ appears too long for one to expect significant anisotropic conductivity; most conductors of this type [2] have metal–metal distances of $<3$ Å. Not surprisingly, Pd•PDC•$4NH_3$ and Pt•PDC•$4NH_3$ exhibited resistivity of $>10^{14}$ ohm as disordered powders.

IR spectra of Pd and Pt•PDC•$4NH_3$ show a strong carboxylate asymmetric stretch absorption at about 1620 $cm^{-1}$ which is at lower frequency than that observed in all of the other PDC compounds. This is in accord with the presence of an uncoordinated carboxylate group [8]. Ni•PDC•$2NH_3$ exhibited an asymmetric carboxylate stretch band in the region of the IR spectrum similar to that observed for the three hydrated PDC polymers. This same absorption in the spectrum of Pd•PDC•$2NH_3$ was at 1630 $cm^{-1}$ which, though lower in frequency, is still not inconsistent with the assumption of a coordinated carboxylate group [8, 10]. There were at least two bands in the IR region associated with symmetric carboxylate stretch (1400–1300 $cm^{-1}$) for all of the ammoniated PDC complexes which makes exact assignment difficult. A similar situation has been observed in IR spectra of metal complexes of pyrazine-2,3-dicarboxylic acid [11].

Both Pd•PDC•$2NH_3$ and Pd•PDC•$4NH_3$ were diamagnetic as expected for square planar palladium. From this observation it is clear that Pd•PDC•$2NH_3$ is not a coordination polymer utilizing all four coordinating sites of the PDC ligand since palladium only rarely exhibits a coordination number greater than four. Despite numerous attempts, crystals of the material large enough for X-ray structure analysis could not be obtained and its exact structure remains speculative. Powder resistivity for Pd•PDC•$2NH_3$ was quite high ($>10^{14}$ ohm). The compound decomposed beginning at 310 °C which was somewhat higher than the initial decomposition temperatures observed for Pt and Pd•PDC•$4NH_3$.

Ni•PDC•$2NH_3$ lost ammonia during TG to yield Ni•PDC which decomposed at significantly higher temperature than Ni•PDC derived from Ni•PDC•$2\frac{1}{2}H_2O$. This may be attributed to the higher degree of crystallinity of Ni•PDC•$2NH_3$ compared to its hydrated analogue [12]. Also noteworthy is the fact that Ni•PDC derived from Ni•PDC•$2NH_3$ apparently decomposed directly to NiO in contrast to the case of Ni•PDC•$2\frac{1}{2}H_2O$ which exhibited oxidation to NiO subsequent to decomposition ($>550$ °C). The magnetic moment of Ni•PDC•$2NH_3$ is consistent with octahedral symmetry about the nickel atom. These data together with the IR spectrum of Ni•PDC•$2NH_3$ mentioned above support designation of the material as a coordination polymer similar to the hydrated PDC polymers. Nevertheless, the compound had a powder resistivity of $>10^{12}$ ohm which may perhaps again be due to lack of long range structural order. Crystals of Ni•PDC•$2NH_3$ large enough for X-ray or single crystal conductivity studies have not yet been obtained.

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