Inorganica Chimica Acta, 101 (1985) L1–L4 L1

Synthesis and Spectroscopic Studies of the Tin(IV)-promoted Hydrolysis of di-2-pyridyl Ketone

DALE L. PERRY*, JOHN L. MARGRAVE and DAVID W. BONNELL**

Department of Chemistry, Rice University, Houston, Tex. 77001, U.S.A.

Received January 22, 1985

The hydrolysis/alcoholysis reaction of di-2-pyridyl ketone (DPK) in the presence of metal ions has been of considerable interest; previous studies have involved transition metal species such as nickel [1–4], iron [2, 4], and cobalt [1, 4, 5] as well as one investigation involving uranium [6]. To date, the mechanism of the reaction is not understood, although it has been proposed on the basis of molecular models that the driving force might involve an $sp^2 \rightarrow sp^3$ transition of the central carbon atom in order to minimize strain and steric interaction within the system [1, 2]. Additional speculation centers around the possible formation of one of the hydroxyl groups of $>C(OH)_2$ bonding to the metal cation, thus resulting in the formation of a tridentate ligand [2].

Research in the chelate chemistry involving this ligand has been almost totally restricted to the non-Main Group complexes, specifically, those involving the first row transition metal ions as the acceptor. In coordination with transition metals, for example, DPK is capable of participating in back π-bonding through electron delocalization of metal t_{2g} electron transfer to the ligand π orbital. Thus, it has been of interest to study its reactions and bonding characteristics in relation to those of the analogous compounds 2,2′-bipyridine and 1,10-phenanthroline, for which there is an extensive known chemistry with metal ions. The spectroscopy of these two ligands in metal complexes is also quite useful in helping distinguishing between interactions of metal ions with the ring nitrogens in DPK versus metal ion interactions with the carbonyl group. The present study makes use of these comparisons.

This investigation also extends the chemistry of di-2-pyridyl ketone with metal ions to tin(IV). With the exception of a brief reference to the tin(II) chloride complex [7], this is the first detailed account of the reaction of the ligand with a Group IVA species. Also, no previous studies of DPK complexes have included the X-ray photoelectron spectral (XPS) data on the oxygen environments in these complexes containing the presumed hydrolyzed carbonyl group.

Experimental

Physical Measurements

Infrared spectra were taken as KBr pellets using a Beckman Model 4250 infrared spectrophotometer with polystyrene as the calibrant. X-ray photoelectron spectra were obtained on an instrument that has been previously described [8]. Samples were pressed into Scotch-brand double sided adhesive tape and were mounted on an eight-position wheel. All spectra were calibrated against the C_{1s} peak, assuming a value of 285.0 eV for the C_{1s} line of contaminant carbon [9]. The samples were pumped down for an extended period of time in an attempt to remove any chemisorbed water.

Elemental analyses were performed by PCR, Inc., Gainesville, Florida. The anhydrous diethyl ether was reagent grade, and it was further dried and stored over sodium metal until used. The ligand di-2-pyridyl ketone was obtained commercially (Aldrich Chemicals) and used without further purification. Tin(IV) chloride (Fisher Scientific), tin(IV) chloride pentahydrate (Baker Chemical), and tin(IV) bromide (Research Organic/Inorganics) were also commercial samples and used as received. Synthetic manipulations were carried out in a nitrogen-filled dry box in order to protect both the tin halides and complexes from extended exposure to moisture. All four complexes were slightly hygroscopic.

Syntheses

$SnCl_4 \cdot C_{11}H_8N_2O$

Tin(IV) chloride was slowly added dropwise to a stirred, cold solution of di-2-pyridyl ketone (0.184 g, 1.0 mmol) in anhydrous diethyl ether. The addition was continued until the precipitation of the adduct was completed, and the complex was allowed to settle. It was then washed several times with diethyl ether, filtered, and dried *in vacuo* for two hours at room temperature. *Anal.* Calcd. for $SnCl_4 \cdot C_{11}H_8N_2O$: C, 29.70; H, 1.80; N, 6.30. Found: C, 30.22; H, 1.92; N, 6.82%.

$SnCl_4 \cdot C_{11}H_8N_2O \cdot 2H_2O$

A solution of tin(IV) chloride pentahydrate (0.351 g, 1.0 mmol) in 20 ml of 95% ethanol was added slowly with stirring to a solution of di-2-pyridyl

---

*Present address: Lawrence Berkeley Laboratory, University of California, Berkeley, Calif. 94720, U.S.A.

**Present address: Chemical Stability and Corrosion Division, National Bureau of Standards, Washington, D.C. 20234 U.S.A.

0020-1693/85/$3.30

TABLE I. Infrared Assignments for Tin(IV)–DPK Complexes.[a,b]

Compound	ν(C=O)	ν(C=C) ν(C=N)	δ(C–H) In plane	δ(C–H) Out of plane
Di-2-pyridyl ketone (DPK)	1675s	1578s	1325s	753s
		1565m		742s
$SnBr_4 \cdot DPK$	1700vs	1610vs	1330m	770s
		1590w		750vs
$SnBr_4 \cdot DPK \cdot 4H_2O$		1607vs	1305s	765vs
		1572w		742w
$SnCl_4 \cdot DPK$	1690vs	1605vs	1330s	765vs
		1582s		745vs
$SnCl_4 \cdot DPK \cdot 2H_2O$		1604vs	1305s	766vs
		1570w		742w

[a] Values in wavenumber, cm^{-1}. [b] Band intensities: vs, very strong; s, strong; m, medium; w, weak.

ketone (0.184 g, 1.0 mmol) in 10 ml 95% ethanol. Stirring of the solution was continued for several minutes during which time the product slowly precipitated. It was subsequently filtered, washed several times with cold diethyl ether, and vacuum dried at room temperature for two hours. *Anal.* Calcd. for $SnCl_4 \cdot C_{11}H_8N_2O \cdot 2H_2O$: C, 27.48; H, 2.50; N, 5.82. Found: C, 26.99; H, 2.37; N, 6.05%.

$SnBr_4 \cdot C_{11}H_8N_2O$

A solution of tin(IV) bromide (0.438 g, 1.0 mmol) in 30 ml of cold diethyl ether was slowly added dropwise to a stirred solution of di-2-pyridyl ketone (0.184 g, 1.0 mmol) in 5 ml diethyl ether. The complex (which formed immediately) was allowed to settle, and the supernatant diethyl ether was then removed. The product was then filtered and dried *in vacuo* at room temperature for two hours. *Anal.* Calcd. for $SnBr_4 \cdot C_{11}H_8N_2O$: C, 21.22; H, 1.29; N, 4.50. Found: C, 21.83; H, 1.39; N, 4.31%.

$SnBr_4 \cdot C_{11}H_8N_2O \cdot 4H_2O$

A solution of tin(IV) bromide (0.438 g, 1.0 mmol) in 30 ml of cold ethanol was slowly added dropwise with stirring to 0.184 g (1.0 mmol) di-2-pyridyl ketone dissolved in 5 ml of 95% ethanol. The product formed slowly over a period of several minutes and was allowed to settle. The supernatant ethanol was drawn off, the complex was washed several times with cold portions of diethyl ether, filtered, and dried at room temperature for two hours under vacuum. *Anal.* Calcd. for $SnBr_4 \cdot C_{11}H_8N_2O \cdot 4H_2O$: C, 20.06; H, 1.82; N, 4.25. Found: C, 21.34; H, 1.71; N, 4.11%.

Results and Discussion

Infrared

The ligand di-2-pyridyl ketone (DPK) can potentially exhibit two modes of coordination as a chelate: through the two ring nitrogen atoms, and less likely, through one of the ring nitrogen atoms *and* the carbonyl group. While the latter type of linkage was reported in an earlier study [10], subsequent work [1] indicated that only N,N-coordination was present for that series of complexes. As a result of the concentrated π-electronic system present in the carbonyl group, adduct formation through it would necessitate a lowering of the carbonyl band found at 1675 cm^{-1} in the free ligand. In the case of N,N-coordination, the pyridine ring vibrational mode, as a result of the high degree of delocalization of the π-electron density, should not experience any high degree of change. The C=O frequency, however, might be expected to increase slightly.

An increase in the carbonyl frequency was indeed observed in this study for two non-hydrated compounds, a 25 and 15 cm^{-1} increase for the $SnBr_4$ and $SnCl_4$ adducts, respectively. The pyridine ring modes, ν(C=C) and ν(C=N), shifted to higher wavenumber in the complexed ligand, with the shift being ~25 cm^{-1} in the case of ν(C=C). This shift was observed in both the anhydrous and hydrated tin(IV) complexes. The ν(C=O) band disappeared in the hydrated complexes (Fig. 1).

The very strong bands at 1521 and 1520 cm^{-1} in the infrared spectra of the anhydrous tin(IV) bromide and chloride complexes, respectively, disappeared on hydration. Previous workers [4] have interpreted strong absorption bands in this region (1530 cm^{-1}, for example, in the case of the iron(III) system) as being proof of N,O-coordination. Other workers [11], however, have observed a strong band at 1512 cm^{-1} in the infrared spectra of the complexes of the bidentate nitrogen donor 2,2-bipyridine with $SnCl_4$ and $SnBr_4$. This band is very close to the 1520–1521 cm^{-1} values observed in this study and was assigned as the totally symmetric ring stretching mode of the pytidine rings. In the complexes studied here, this vibrational mode appar-

TABLE II. Binding Energies of Tin(IV) Halide–DPK Complexes.[a]

Compound	Sn(3d$_{5/2}$)	N(1s)	O(1s)	Br(3d$_{5/2}$)	Cl(2p$_{3/2}$)
$SnBr_4$·DPK	487.2	400.2	532.1	69.6	
$SnBr_4$·DPK·$4H_2O$	487.1	400.9	533.4	69.5	
$SnCl_4$·DPK	487.8	400.6	532.2		198.4
$SnCl_4$·DPK·$2H_2O$	487.6	400.4	533.3		198.5

[a] Value are in electron volts (eV) and are referenced to the contaminant carbon line: $C_{1s} \equiv 285.0$ eV.

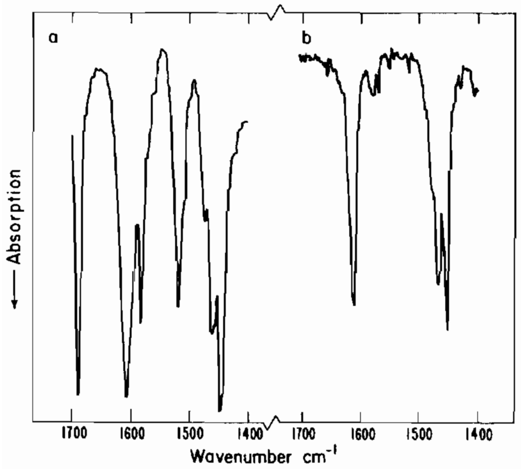

Fig. 1. Infrared spectra of (a) $SnCl_4$·DPK and (b) $SnCl_4$·DPK·$2H_2O$ in the 1700–1400 cm^{-1} region.

ently becomes infrared inactive on hydration of the complexes. Spectra of the anhydrous and hydrated $SnCl_4$ complexes shown in Fig. 1 illustrate this.

Complexation of a metal ion with di-2-pyridyl ketone which yields an alcoholated or hydrated species (such as the one reported here) also gives an infrared spectrum which does not contain a C=O stretching frequency. Previous workers [1, 2] have suggested the following reactions with alcohols, water, and the carbonyl group of the ligand:

$$C{=}O + ROH \longrightarrow C(OH)(OR) \qquad (1)$$

$$C{=}O + H_2O \longrightarrow C(OH)_2 \qquad (2)$$

Any reactions such as these with the carbonyl group would effect a concomitant strengthening of the bonding in the pyridine ring system and thus increase the ring frequencies. As mentioned above, this increase was observed for all four complexes, with the magnitudes of the shift comparing very favorably with those previously reported for other metal systems [1–3].

X-Ray Photoelectron

The tin-3d$_{5/2}$ lines of the complexes in this study exhibited values that ranged from 487.1 to 487.8 eV (Table II). The value of 487.2 eV recorded for $SnBr_4$·DPK is in good agreement with that of 487.6 eV previously reported for $SnBr_4$·2,2′-bipyridine [12]. As shown by Fehlner and co-workers [14], however, most tin(IV) complexes involving ligands with oxygen, nitrogen, and sulfur donor atoms have tin binding energies in this range, clearly demonstrating the core electron binding energies to be insensitive to the bonding environment of the tin. For example, the bis(triphenylphosphine oxide)-tin(IV) bromide complex [12] has a tin-3d$_{5/2}$ line at 487.7 eV, almost identical to the value of 487.6 eV reported here for the bidentate di-2-pyridyl ketone nitrogen donor in $SnCl_4$·DPK·$2H_2O$. The core binding energies tabulated here consequently give very little insight into the bonding of the present tin complexes.

The nitrogen-1s lines range from 400.2 eV, in very good agreement with those reported earlier [12]* for similar complexes of 2,2′-bipyridine and other nitrogen donor ligands. The nitrogen-1s binding energy in di-2-pyridyl ketone is 398.4 eV. Thus, the increase in binding energy is ~2 eV on coordination of the ligand to tin(IV), the same magnitude of change in the nitrogen-1s line binding energy as with the coordination of 2,2′-bipyridine to tin(IV).

The bromine-3d$_{5/2}$ values of 69.5 and 69.6 eV for the $SnBr_4$ complexes are those that would be expected for terminally bonded, coordination sphere bromide ligands [13]. The case of the chloride ions is less clear in that the 198.6 eV chlorine-2p$_{3/2}$ line for $SnCl_4$·DPK·$2H_2O$ is slightly higher than the 198.5 eV value accepted for inner coordination sphere chlorine atoms [13]. These workers [13] have noted, however, that the irradiation and high vacuum inherent in the XPS experiment can affect the bonding status of chloride ions in coordination compounds, especially those containing water. This would probably apply even more to the compounds in this study, which are hygroscopic by nature. Deterioration such as this was not readily apparent

---

*All binding energies from other studies, quoted here for comparison to the binding energies in this study, have been normalized to the contaminant $C_{1s} \equiv 285.0$ eV line using C_{1s} values reported by the authors of these studies.

from the data obtained here, since the compounds gave spectra which were not a function of the time they were irradiated.

The oxygen-1s lines for the hydrated and anhydrous tin(IV)–DPK complexes should be useful in distinguishing between the unreacted carbonyl and the hydrated or alcoholated species shown in eqns. 1–2. The binding energies, along with the peak widths, were indeed different for the two types of complexes here. $SnBr_4$·DPK and $SnCl_4$·DPK exhibited oxygen binding energies of 532.1 and 532.2 eV, respectively, values that are expected for organic carbonyl groups [14]. The hydrated compounds had oxygen-1s lines at higher binding energies, lines which were also broader (~0.3 eV broader). These higher binding energies are in agreement with a hydroxide species [14], but they are also in agreement with a hydroxide species [14], but they are also in agreement with simple lattice or coordinated water molecules [15]. Again, because of the hygroscopic nature of these compounds, the XPS parameters observed for the present series of complexes may only reflect a small surface layer of adsorbed water. The slight line broadening might also indicate multiple oxygen species which appear as superimposed lines on the spectrum. The results here should therefore be weighed against this possibility.

Acknowledgements

The authors wish to thank the Robert Welch Foundation and the National Science Foundation for support of this work. One of the authors (D.L.P.) wishes to thank the National Science Foundation for a postdoctoral fellowship.

References

1 M. C. Feller and R. Robson, *Aust. J. Chem., 21,* 2919 (1968).

2 M. C. Feller and R. Robson, *Aust. J. Chem., 23,* 1997 (1970).

3 J. D. Ortego and D. L. Perry, *J. Inorg. Nucl. Chem., 35,* 3031 (1973).

4 V. Rattanaphani and W. R. McWhinnie, *Inorg. Chim. Acta, 9,* 239 (1974).

5 J. D. Ortego, D. D. Waters and C. S. Steele, *J. Inorg. Nucl. Chem., 36,* 751 (1973).

6 G. C. Pappalardo and A. Seminara, *J. Inorg. Nucl. Chem., 38,* 1993 (1976).

7 D. L. Perry and R. A. Geanangel, *J. Inorg. Nucl. Chem., 36,* 205 (1975).

8 D. L. Perry, D. W. Bonnell, G. D. Parks and J. L. Margrave, *High Temp. Sci., 9,* 85 (1977).

9 W. L. Jolly, *Coord. Chem. Rev., 13,* 47 (1974).

10 R. R. Osborne and W. R. McWhinnie, *J. Chem. Soc. A:,* 2075 (1967).

11 S. S. Singh and C. B. S. Sengar, *Isr. J. Chem., 7,* 471 (1969).

12 P. A. Grutsch, M. V. Zeller and T. P. Fehlner, *Inorg. Chem., 12,* 1431 (1973).

13 V. I. Nefedov, *J. Electron Spectrosc. Relat. Phenom., 12,* 459 (1977).

14 B. J. Lindberg, K. Hamrin, G. Johansson, U. Gelius, A. Fahlman, C. Nordling and K. Siegbahn, *Phys. Scr., 1,* 286 (1970).

15 D. C. Frost, A. Ishitani and C. A. McDowell, *Mol. Phys., 24,* 861 (1972).